

# Advanced pH Measurement and Control

3rd Edition

Lab: Good Feedback Model

Process Gain:

Time Constant:

Deadline:

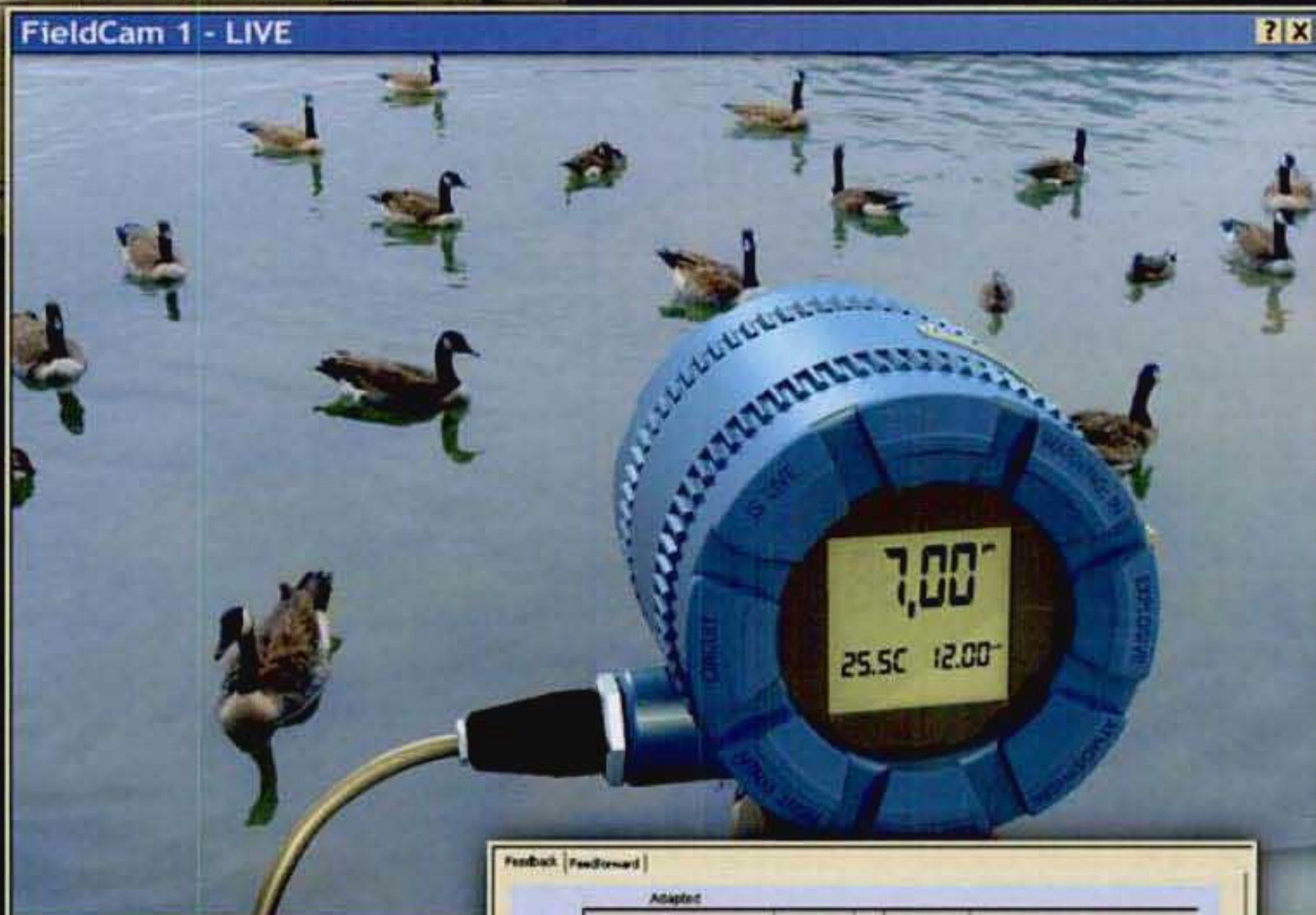
Status: Good

Operation

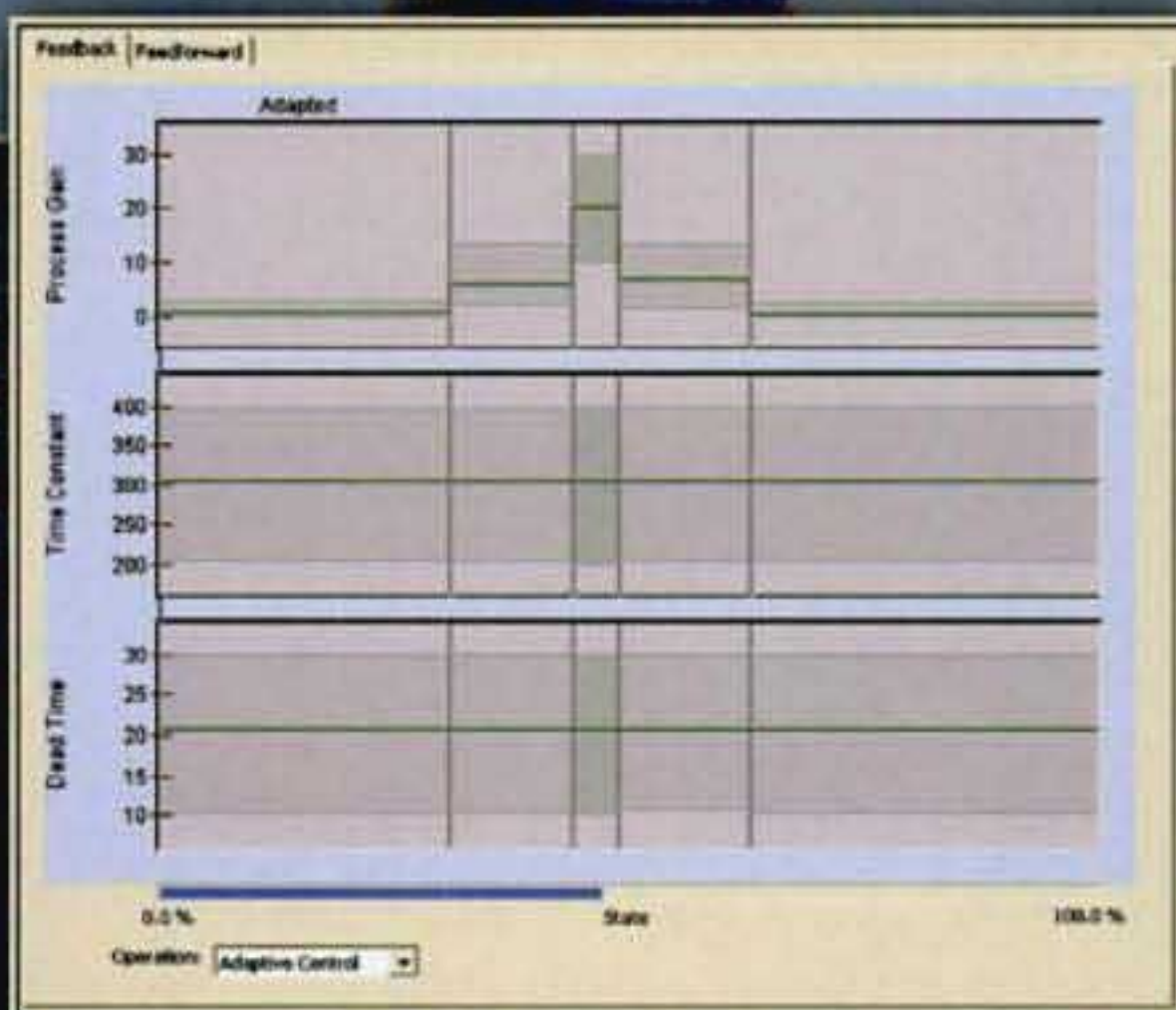
Region: Region 1

Status: Good

Type: Adaptive Control



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## Preface to the Third Edition

The pH electrode offers by far the greatest sensitivity and rangeability of any industrial process measurement. To realize the full potential of this opportunity requires extraordinary performance of mixing equipment, control valves, reagent delivery systems, flow meters, control system design, and controller tuning. This book is designed to cover all of the bases but not get the user lost in the details. Since each of these topics could be a book in itself, the emphasis here is on cutting straight to the chase of concepts critical for a successful pH system. Key insights and rules of thumb are inserted to congeal principles and practices that address the essential requirements of pH applications. The book should appeal to both the generalist and the specialist. This book is designed to bring together the chemist, control engineer, instrument technician, process engineer, and project manager to literally and figuratively put them on the same page.

*Chapter 1 – The Essentials* provides a concise overview of what makes pH applications unique. It covers the total system requirements and is designed for the widest possible audience. It uses an adventurous style and analogies that should help make this chapter interesting enough to read from start to finish. The other chapters follow up on the seeds planted here and are intended to be used more as a reference for the design of each part of a pH measurement and control system.

*Chapter 2 – The Chemistry* gets into the engineering units and the conversion of the abscissa of the titration curve into ratios that are useful for pH system analysis and design. It tackles the effect of the crowding of ions at higher concentrations on pH. This should help a control engineer or technician communicate with the process engineer and chemist and vice versa, effectively use a lab titration curve, and understand how pH is affected by the concentrations of acids, bases, and salts and process temperature. The chapter concludes with development of charge balance models that coupled with Coriolis flow meters enable the development of fast and reliable online pH estimators.

*Chapter 3 – Titration Curves* discusses how the steepness of the slope in the operating region determines the difficulty of the application and how it changes with composition. Accurate titration curves are the key to pH system design, analysis, online pH estimators, online process efficiency indicators, and real time optimization. Yet they are fraught missing or misleading information and notorious for graphical deception. The goal of this chapter is to deal with these issues and detail the requirements to generate a useful titration curve in the laboratory, by a charge balance model, or online in the field.



*Chapter 4 – Electrodes* is the heart of the text because ultimately it all begins and ends with performance of the measurement. If you don't get this right, nothing else matters. This chapter starts with a proper dose of reality to help the user sort out fact from fiction. Reality is not pretty but it can prevent a lot of false expectations and the consequential astonishments and atonements. This chapter proceeds with a survey of the myriad of measurement and reference electrode designs. The hard data to date is primarily in buffer solutions or developed by the manufacturer. There is a serious need for testing by a third party of all major electrode designs for the wide range of conditions and requirements encountered in the food and beverage, biochemical and pharmaceutical, the chemical and petrochemical, and water treatment processes. Armed with as much information that can be gleaned from assumptions made and features described in the literature and personal application experience, the chapter proceeds to provide as much guidance as possible in the selection, installation, calibration, and troubleshooting of electrodes, and the use of smart transmitters.

*Chapter 5 – Mixing Equipment* makes sure the biggest capital investment in a pH system is wisely spent. The chapter is designed to get the control engineer, mixing specialist, and process engineer in tune with the dynamics and extraordinary mixing requirements demanded by exceptionally steep titration curves and incredibly small reagent flows. This chapter focuses on the implications of the magnitude of a plug flow volume and its size relative to a back mixed volume. Simple equations are presented to estimate the dead time, time constant, and the attenuation capability of a volume. This should help the user pick the correct type and size of mixing equipment and recognize when an existing pH loop is doomed to failure.

*Chapter 6 – Control Valves* deals with the many significant issues that arise from trying to precisely throttle a tiny reagent flow. It focuses on the challenges of manufacturing tolerances, transitions between turbulent and laminar flow, plugging, and stick-slip when trying to make extremely small changes in a flow that might already be the size of a leakage flow for normal sized valves. The chapter shows how meeting the resolution spec found from the titration curve can minimize the cost of mixing equipment and generally satisfy the rangeability requirement. It also discusses how to minimize the nonlinearity, stick-slip, and dead time introduced by split ranging. It concludes with a discussion of the problems and solutions in the application of metering pumps and lime feeders.

*Chapter 7 – Reagents* delves into reagent delivery system design in terms of adding dead time and a high-level view of the characteristics of common reagents. It provides some general guidelines on the strength, phases, and



consistency of reagents. Physical property handbooks and databases are the best source of more detailed information on reagents.

*Chapter 8 – Control Systems* digs into the first love of the authors. For us, the book saves the best for last. It covers the basics of feedback, feedforward, and cascade control and then launches into the more sophisticated techniques such as linear reagent demand, adaptive, model predictive, and advanced batch control. It introduces the new opportunities afforded by online titration curves for online pH estimators, and real-time optimization. The chapter realizes that these topics may only be of passing interest in the route to a successful pH application so the reader is directed to the references noted for the details of the technologies. The chapter then dives into equations and methods for estimating controller tuning and loop performance and concludes with a summation of the best practices and the logic for choosing the best control strategy and technology.

Appendices G and H were added as a finishing touch to summarize the guidelines and the use of the enclosed computer programs that can help the user achieve the best design.

## **ISA's Independent Learning Modules**

This book is an Independent Learning Module (ILM) as developed and published by ISA. The ILMs are the principal components of a major educational system designed primarily for independent self-study. This comprehensive learning system has been custom designed and created for ISA to more fully educate people in the basic theories and technologies associated with applied instrumentation and control.

Paul W. Murrill

Consulting Editor, ILM Series



# **Chapter 1: The Essentials**



# Chapter 1

## The Essentials

### 1-1. The Heart of the Matter

This chapter is designed to provide everything you really need to know about pH in a couple of hours since time is a premium and edification a luxury. This introduction gets you started in the right direction. The succeeding chapters are layered with a level and degree of details that range from the novice to the expert.



The pH electrode offers by far the greatest sensitivity and rangeability of any measurement. To make the most of this capability requires an incredible precision of mixing, reagent manipulation, and nonlinear control. pH measurement and control can be an extreme sport.

The logarithmic relationship between pH and hydrogen ion activity as seen in Equation 1-1b offers the ability to measure hydrogen ion concentration from 1 to  $10^{-14}$  over the 0 to 14 pH scale range. In fact, pH measurements below 0 and above 14 are also possible, which extends the rangeability beyond 14 orders of magnitude.

$$a_H = 10^{-\text{pH}} \quad (1-1a)$$

$$\text{pH} = -\log(a_H) \quad (1-1b)$$

$$a_H = \gamma \cdot c_H \quad (1-1c)$$

where:

$a_H$  = hydrogen ion activity (gm-moles per liter)

$c_H$  = hydrogen concentration (gm-moles per liter)

$\gamma$  = activity coefficient (1 for dilute solutions)

pH = negative base 10 power of hydrogen ion activity

The hydrogen ion activity is the effective concentration and is a measure of the ability of the hydrogen ion to move and combine with other ions. For dilute solutions, the effective and actual concentrations are equal and the activity coefficient is one. For solutions with high concentrations of ions, the crowding and presence of other charges reduces the activity coefficient to less than one and the effective concentration is less than the



actual concentration. For solutions with less than 90% by weight water or more than 5% by weight salt, the pH becomes a noticeable function of water and salt besides hydrogen ion concentration. Certain salts, such as NaCl, also affect the millivolt potential developed by the measurement and reference electrodes. The ions from the dissociation of acids and bases also have activity coefficients that affect the charge balance and hence the pH.

The product of the hydrogen and hydroxyl ion concentrations must equal 10 raised to the minus power of the water dissociation constant ( $pK_w$ ) per Equation 1-1d for water solutions. The  $pK_w$ , and thus the actual solution pH, is a function of the process temperature. In the pH titration curve chapter we will find out how other dissociation constants can cause the solution pH to change. It is important to realize that the standard temperature compensator corrects for the temperature effect on the millivolt potential developed by the electrode and not for the changes in the actual pH with temperature. Smart transmitters have recently added the option for the user to program for the correction of the effect of temperature on the solution pH. Except for dilute strong base solutions above 7 pH, the exact relationship between temperature and solution pH is not generally available and needs to be developed from lab tests.

$$c_H * c_{OH} = 10^{-pK_w} \quad (1-1d)$$

where:

- $c_H$  = hydrogen ion concentration (gm-moles per liter)
- $c_{OH}$  = hydroxyl ion concentration (gm-moles per liter)
- $pK_w$  = negative base 10 power of the water dissociation constant (14.0 at 25°C)



**The actual solution pH changes despite a constant hydrogen ion concentration because of changes in dissociation constants with process temperature, and activity coefficients with ionic strength and water content.**

At the neutral point, the concentration of hydrogen and hydroxyl ions is by definition equal. If the temperature is 25°C, the  $pK_w$  is 14.0, which means the pH is 7 and the hydrogen and hydroxyl ion concentrations are both  $10^{-7}$ . Table 1-1a shows how the hydrogen and hydroxyl ion concentrations change by a factor of 10 for each pH unit.

Table 1-1a illustrates the heart of the matter. No other type of commonly used measurement covers such a tremendous range. Also, the pH electrode can respond to changes as small as 0.01 pH, which means the pH



measurement can track changes as minute as 0.000000005 in hydrogen ion concentration at 7 pH. No other commonly used measurement has such tremendous sensitivity. As with most things in life, you don't get something for nothing!

Table 1-1a. Hydrogen and Hydroxyl Ion Concentrations in a Water Solution at 25°C

pH	Hydrogen Ion Concentration	Hydroxyl Ion Concentration
0	1.0	0.0000000000000001
1	0.1	0.000000000000001
2	0.01	0.00000000000001
3	0.001	0.0000000000001
4	0.0001	0.000000000001
5	0.00001	0.00000000001
6	0.000001	0.000000001
7	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1
14	0.00000000000001	1.0

The rangeability and sensitivity capabilities cause associated control system design problems that can seem insurmountable [Ref. 1.1]. It is important to realize that these problems are due to attempting a level of performance in the pH process in terms of concentration control that goes well beyond the norm. For a strong acid and strong base control system, the reagent valve must have a rangeability greater than 1,000,000:1 for an incoming stream that varies between 0 and 6 pH and a set point at 7 pH. The stick-slip of the same control valve must be less than 0.00005% to control within 1 pH of the 7 pH set point. How then is this possible? Such strong acid and base systems are controlled by approaching the set point in stages and using successively smaller precision control valves. The multiple state requirement of pH control can be visualized by comparing it to trying to sink a golf ball in the hole on a green. The distance between the tee and the green presents the rangeability requirement and the size of the hole compared to the distance represents the sensitivity requirement. For the above strong acid and strong base system, the tee would be about a million yards from the green. A hole in one is possible. Using the same



large control valve at each state is like the joke about the gorilla who drives the green in one stroke but then uses his driver again and hits the ball the same distance when he tries to putt the ball in the hole.

The process gain at a given pH set point is best visualized as proportional to the slope of the titration curve. The titration curve is a plot with pH for the Y axis and the ratio of reagent to influent concentration, volume, or flow for the abscissa. For a strong acid and base system, the process gain between 6 and 7 pH is 6 orders of magnitude larger than the process gain between 0 and 1 pH. Figure 1-1a shows a titration curve for a strong acid and strong base at 25°C. The curve appears to be a vertical straight line between 2 and 12 pH and symmetrical about the neutral point where the concentration of hydrogen and hydroxyl ions are equal. However, a zoom in on the straight line reveals another S-shaped titration curve. Successive zooms centered on 7 pH should always yield additional S-shaped curves, as seen in Figures 1-1b and 1-1c, since the slope is continuously changing by a factor of 10 for each pH unit deviation from 7 pH. However, most titration curves will not show this true behavior because there are not enough data points. It is quite common for there to be only a couple of data points in the neutral region where the slope is steepest even though this is the location of the set point and hence the area of greatest interest for environmental and biological systems. Also, many users overlook or inadequately define the abscissa. For example, if management looks at Figure 1-1c ignoring the X scale, the curve looks relatively harmless and they will wonder, "What is the big deal?" Graphical deception is a common problem in pH systems.

A lab titration consists of drops being added to a beaker with a fixed sample volume and composition until an end point is reached. This is similar to traditional batch pH control. If the chemist says it is too difficult to make the drops small enough during titration to add enough data points in the neutral region to see the curvature, this is a red flag. It is going to be even more difficult in the plant to adjust these small changes in dosage to hold a set point, particularly for upsets. In continuous pH control, there is a variable feed and discharge flow and a need to keep the discharge always at a set point. It is analogous to a chemist having to vary the number/size of small drops to a beaker with a hole in the bottom and a variable make up flow and composition by just looking at the pH meter.

For a control loop to respond equally well for all excursions along the 0 to 14 pH scale, the controller gain would have to change in an equal and opposite direction to the pH process gain so that the loop gain is constant. Using multiple stages to limit the pH excursions to a small region around set point reduces the change in gain seen by the controller. The set points are incremented between the influent and desired final pH so that the



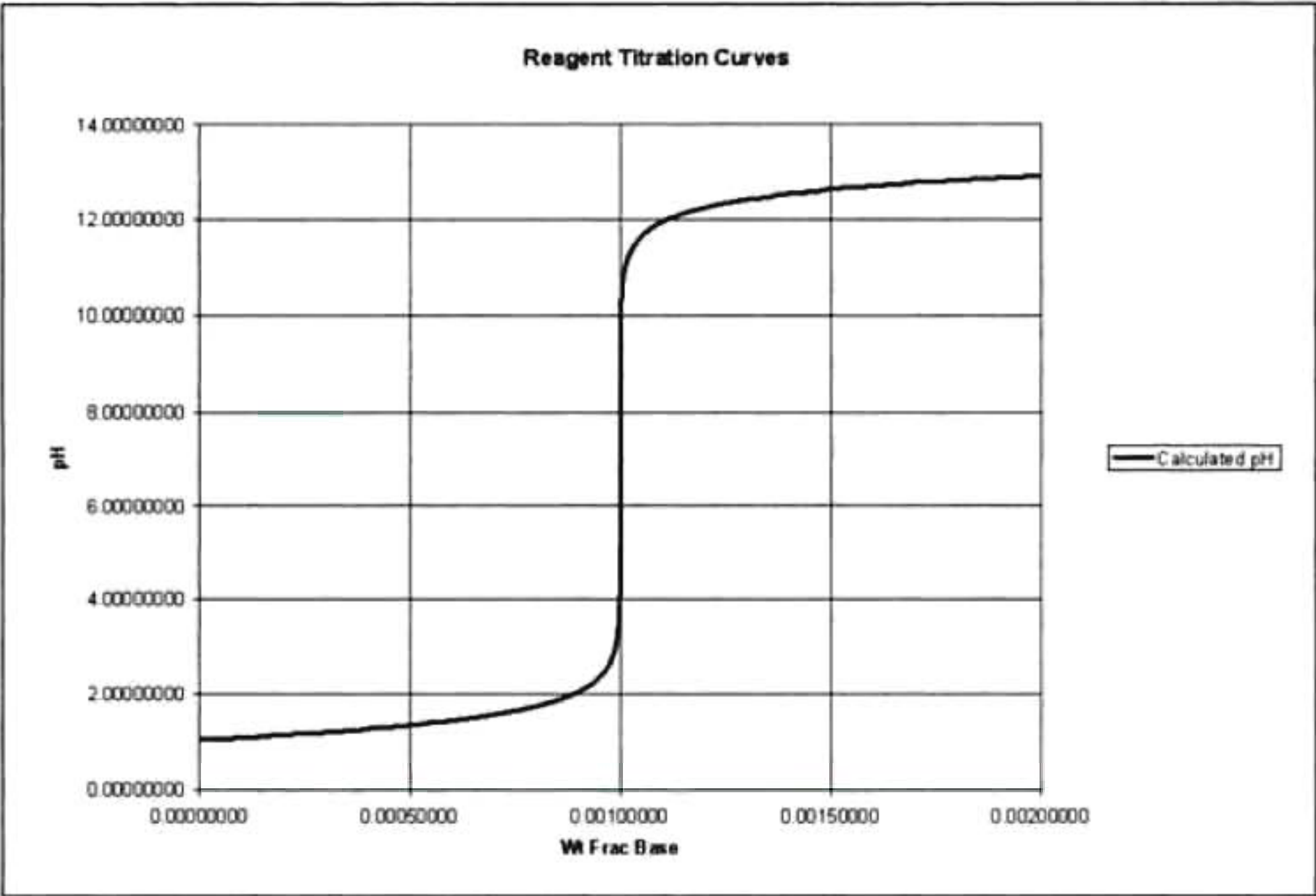


Figure 1-1a. Strong Acid and Base Titration Curve for the Entire Operating Range

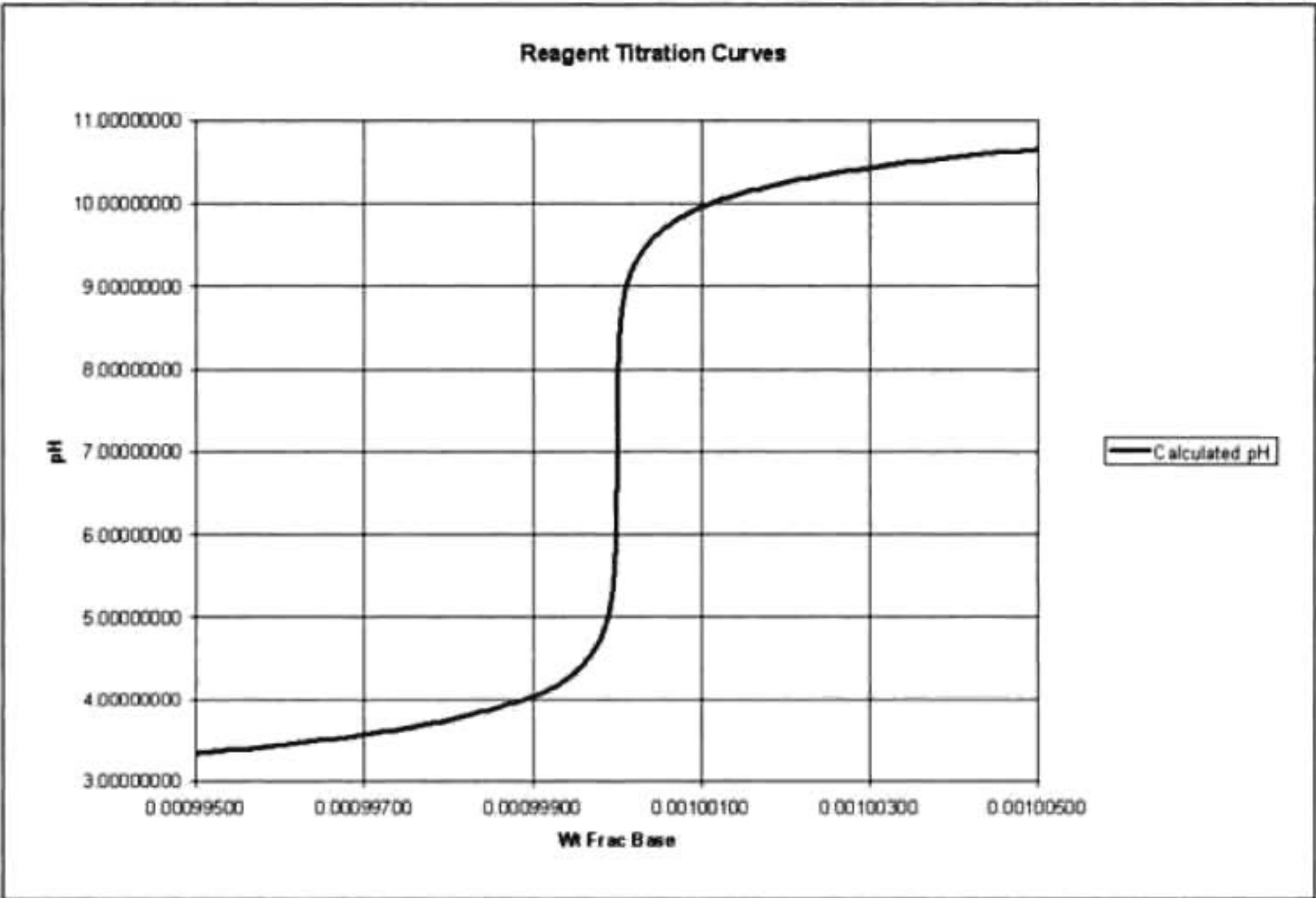


Figure 1-1b. Strong Acid and Base Titration Curve that Zooms in on 3 to 11 pH Range

distance in acid or base concentration between the influent and set point pH is reduced for each control loop [Ref. 1.1].



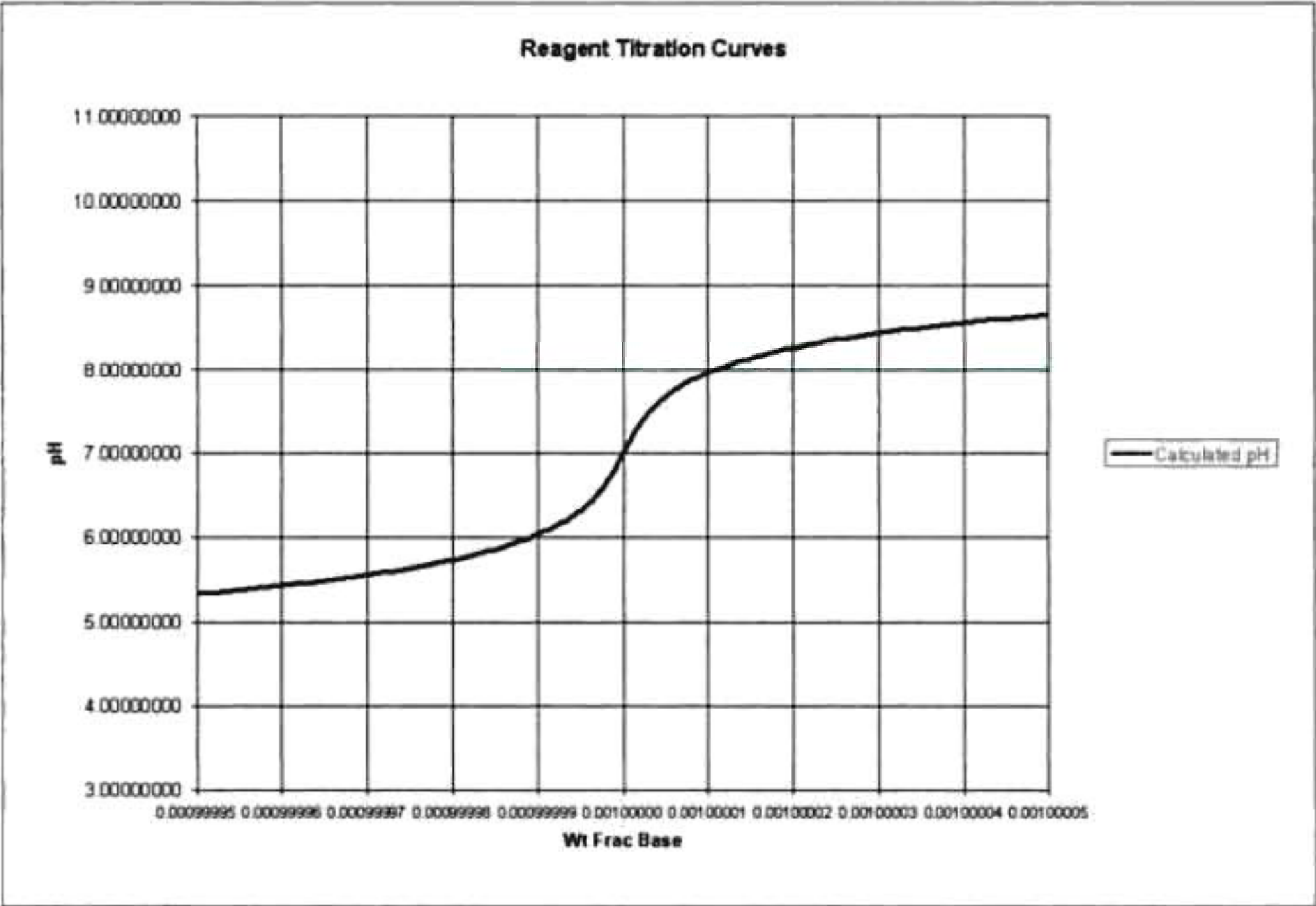



Figure 1-1c. Strong Acid and Base Titration Curve that Zooms in on Neutral Region

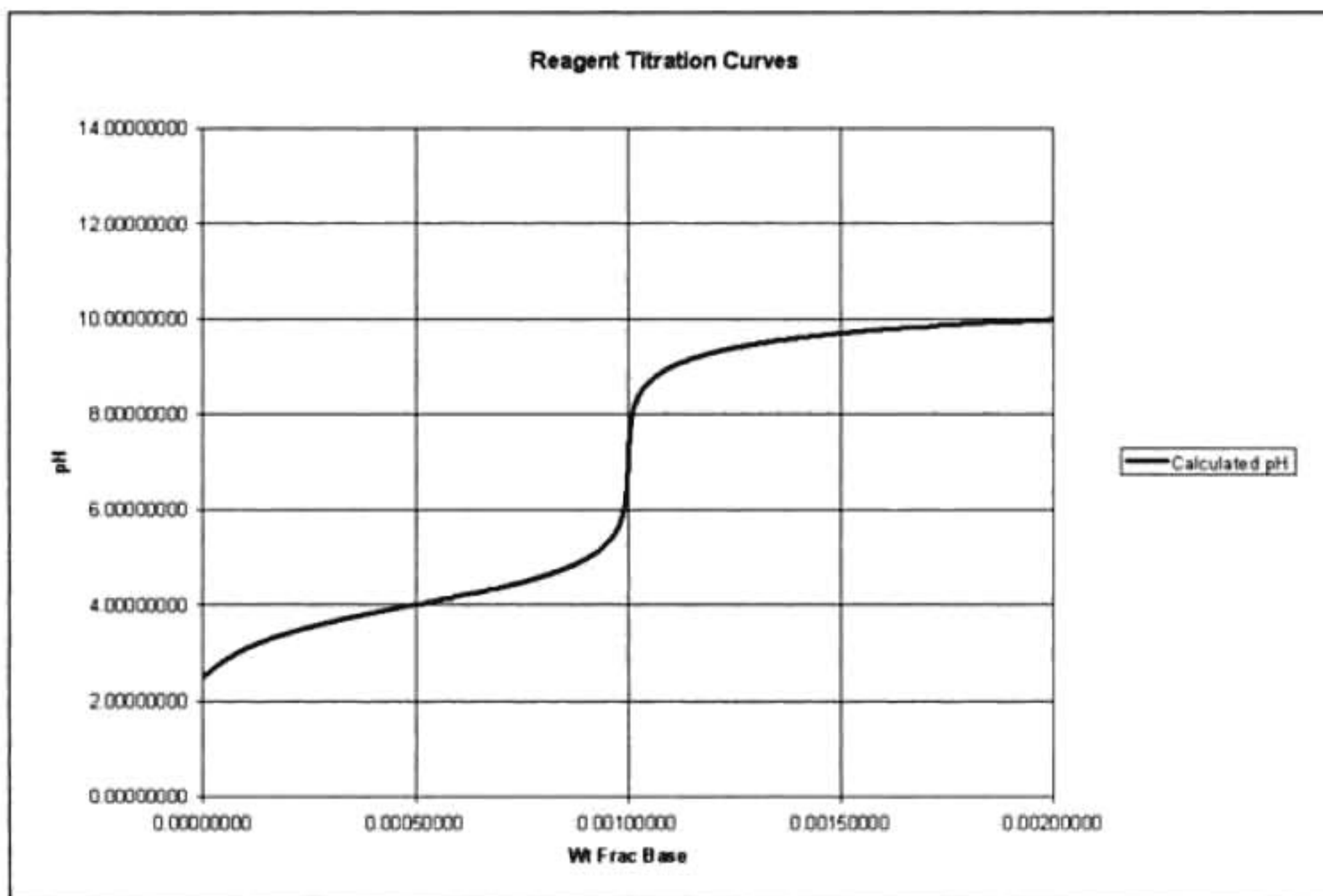


There are no straight lines in a titration curve. A zoom in on any supposed line should reveal another curve if there are sufficient data points.

Fortunately, many pH systems have weak acids and bases that flatten out various portions of the titration curve to provide a buffering effect. The overall difficulty is reduced especially if the set point ends up residing on one of these plateaus as shown in Figure 1-1d for a weak acid and base [Ref. 1.1]. The natural buffering of surface and ground waters from carbonates can change your mood from suicidal to merely depressed when the actual curves are compared to theoretical titration curves with pure water. Titration curves of fabricated samples will be much steeper than the titration curves of actual process samples, especially if the lab uses deionized water instead of plant water.

For the control system to work, special attention must be paid to designing and installing the electrodes, transmitter, controller, control valve(s), piping, and mixing equipment. A mistake in the design or installation of any component in the loop can cause the control system to not only fail but fail miserably. The process, mechanical, and instrument engineers all must be alert to special system requirements from the inception of the project. The top 12 mistakes are summarized in Table 1-1b. Ten of these





**Figure 1-1d. Weak Acid and Base Titration Curve with Flattened Areas (Plateaus)**



The flatness of the titration curve at the set point has the greatest effect on the tightness of pH control. The next most important effect is the distance between the influent pH and the set point.

are illustrated in Figure 1-1e, which shows the use of a horizontal tank, gravity flow reagent, and a ball valve without a positioner.

The titration curve is the essential tool for determining the nonlinearity, sensitivity, and rangeability requirements that are important for every step from project definition through sustaining installed performance. It determines the investment required, the design details, and the expected efficiency, operability, and maintainability. Without a titration curve, you are flying blind [Ref. 1.1 and 1.2].



*The first step in designing a pH system is to generate a titration curve at the process temperature with enough data points to cover the range of operation and show the curvature within the control band (absolute magnitude of the difference between the maximum and minimum allowable pH).*



Table 1-1b. Top Twelve Mistakes Made Every Day in pH System Design

1.	Incorrect or missing titration curve
2.	Absence of a plan to handle failures, start-up, and shutdown
3.	Insufficient number of stages of neutralization (inadequate rangeability and sensitivity)
4.	Improper vessel geometry and agitation patterns (excessive equipment dead time)
5.	Backfilled reagent dip tube (excessive reagent delivery delay)
6.	Incorrect location of reagent injection point (short circuiting)
7.	Gravity flow reagent (excessive reagent delivery delay)
8.	Incorrect location of reagent control valve (excessive reagent delivery delay)
9.	Control valve with excessive stick-slip (poor sensitivity and excessive variability)
10.	Electrodes submersed in vessel (coating and maintainability problems)
11.	Electrodes located in pump suction (bubbles, clumps, and wrenches)
12.	Electrodes located too far downstream (excessive measurement delay)

1-2. Stage Fright

With the pressure on minimizing capital costs, a project may sell themselves short on the number of stages required. The basic rule from the 1970s was that for every two pH units that the influent is away from set point requires one well mixed tank. For example, if the set point was 7 pH, one stage for an influent at 5 pH, two stages for an influent at 3 pH, and three stages for an influent at 1 pH would be required. The modern day version of this old rule would reduce the requirement by one stage if feedforward control or signal linearization could be effectively used or if the set point could be moved to a flatter portion of the titration curve. Today, three stages are rarely used. Even the most difficult systems are tackled by an inline system for the first stage followed by a well-mixed vessel for the second stage.

One of the most frequently missed opportunities in terms of dramatically reducing the difficulty of control and saving on reagent usage is to shift



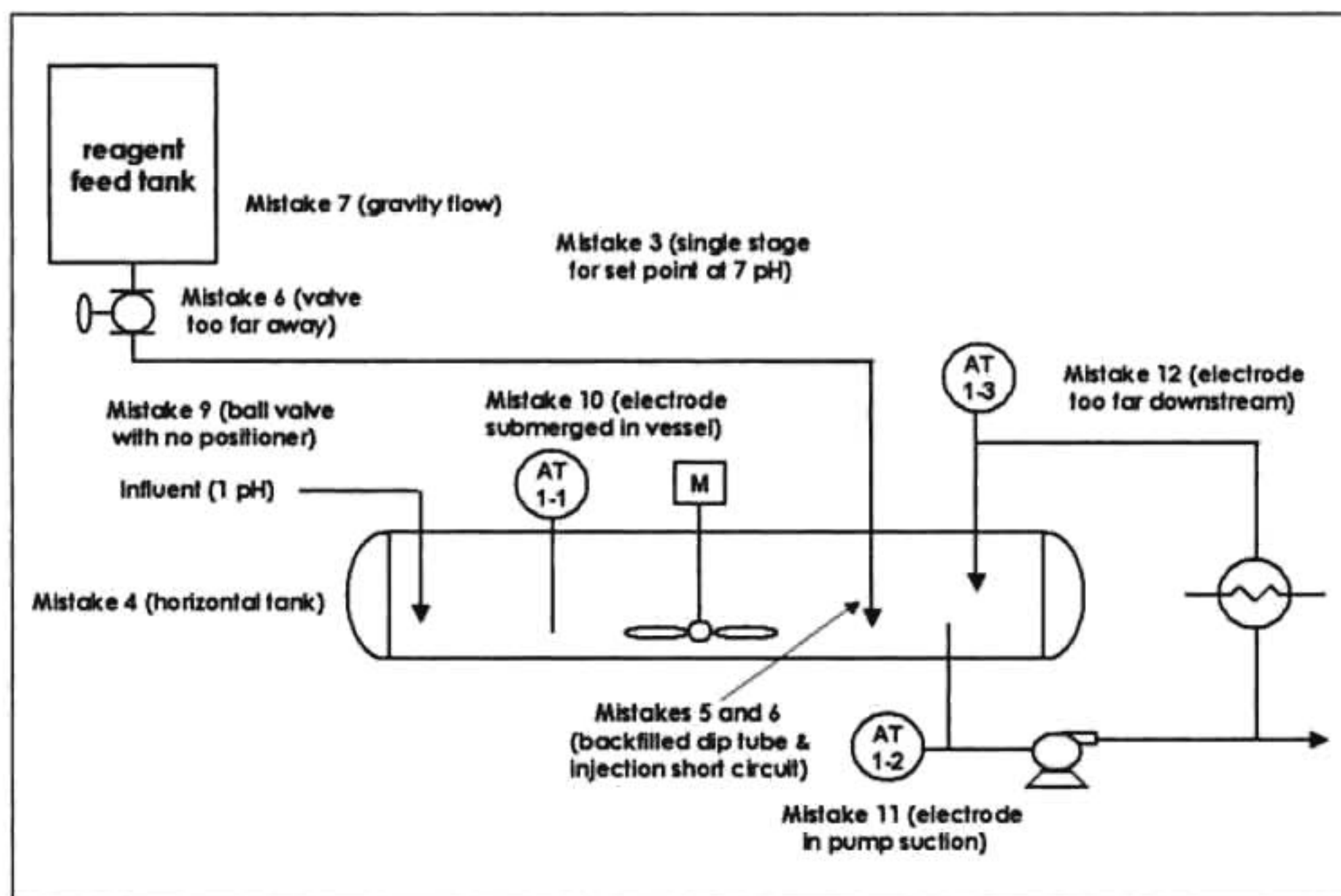


Figure 1-1e. Examples of Mistakes Made Every Day in pH System Design



The titration curve is the essential tool for every aspect of pH system design and analysis.

the set point away from the center to the edge of a control band where the slope is flatter. While it may seem to be wrong in terms of flirting with the edge, the large oscillations from set points at the steepest point waste reagent and the sluggish tuning put you at a greater risk of going over the edge. For example, many environmental systems must keep the effluent between 2 and 12 pH to avoid its classification as hazardous waste. However, a set point at 7 pH is the wrong choice and may lead to oscillations between 2 and 12 pH. A much better choice would be an optimized set point of 4 pH for acidic influent and 10 pH for basic influent. You can warm up to the idea by seeing the tremendous difference at an operating point of 5 or 9 pH. You can be a hero by going into a control room and simply changing the set point to a flatter part of the curve and increasing the controller gain. Of course, the loop probably was not stable to begin with at 7 pH, so the better set point does not mean you can increase the gain by a factor of 10 per pH unit even though it might be a strong acid and base.



*For a set point on the steepest part of the titration curve, one stage of neutralization is needed for every two pH units away from set point. Accurate feedforward control and precise valves can eliminate one stage.*





**There is a huge opportunity to reduce reagent usage and capital investment by simply moving the set point to a flatter part of the titration curve and closer to the influent pH.**

In the 1980s, it was found you could substitute a static mixer for the first vessel by using an appropriate measurement filter. A static mixer is a piece of pipe with baffles or tabs that subdivides the flow stream to provide radial mixing. A centrifugal pump can serve the same purpose. However, these inline mixers provide little to no back mixing or smoothing. Consequently, the process dead time is larger than the process time constant, which leads to large peak errors for fast upsets and a tendency for the loop to oscillate. Originally it was thought that the large oscillations meant you could only use inline mixers on the flat portions of curves or for large control bands. However, since the period and recovery time is fast for a well-designed inline system, a judiciously applied measurement filter can allow a pH loop to control the average of the oscillations if there is sufficient volume downstream to smooth out the concentration fluctuations [Ref. 1.1 and 1.2].

Stick-slip is the most frequent source of oscillations in pH control. For example, if the stick-slip is 0.2%, the reagent valve capacity 1 gpm, and the influent flow 1000 gpm, then the amplitude of the oscillation in the ratio of reagent to influent flow is 0.000002 along the X axis of the titration curve. For a strong acid and base system, this could translate to an oscillation of 4 to 10 pH around a 7 pH set point whenever the loop is in automatic.

Stick is the percent change in valve signal needed to make the trim move and is caused by friction in the packing and trim sealing surfaces. Slip is the change in position, once the valve trim moves, again in percent of the signal span. The slip in a properly designed valve is about equal to the stick and sets the resolution capability of the valve.

For large valves, the percent stick-slip translates to a large error in reagent flow. Control strategies discussed in Chapters 6 and 8 have been developed to position a large reagent valve by feedforward and valve position control to keep a small valve in a good throttle range. Manipulating coarse and fine adjustment valves can eliminate a stage.



***Using a static mixer or pump as a fast inline pH system can eliminate the need for a well mixed vessel for the first stage even for a set point on the moderately steep part of a curve by the judicious use of a signal filter.***



For  $\tau_o > T_o$  :

$$A_o = A_i * \frac{T_o}{2 * \pi * \tau_o} \quad (1-2a)$$

where:

- $A_o$  = output amplitude (pH or concentration)
- $A_i$  = input amplitude (pH or concentration)
- $T_o$  = oscillation period (minutes)
- $\tau_o$  = open loop time constant (minutes)

The open loop time constant in Equation 1-2a is either the digital signal filter time in a Distributed Control System (DCS) for smoothing out pH oscillations and noise or the residence time for a well-mixed vessel for smoothing out concentration oscillations. Equation 1-2a is useful for estimating the size of vessels needed to smooth out stick-slip and the size of a signal filter to keep short term pH fluctuations within the control band [Ref. 1.3]. For example, if the oscillation period of pH noise is 0.012 minutes, a digital filter of 0.04 minutes would reduce the noise amplitude by a factor of 20.

It is critical that filters be judiciously used because they add delay to the response to unmeasured load upsets and provide an illusion of better control by providing an attenuated version of the real world. They should only be used to help screen out transients that are so fast they will be smoothed out by a downstream volume and any response by a controller would potentially do more harm than good. It is also important to realize that there will be an offset in the actual pH of the effluent compared to the average pH signal because of measurement errors and noise and any non-symmetry of the titration curve about the set point. The effect can be estimated by translation of the oscillations on the titration curve. Normally the offset is relatively small (less than 1 pH) and can be reduced by a simple bias of the upstream set point [Ref. 1.2]. The use of process variable signal characterization to imbed the titration curve and create a linear reagent demand controller described in Chapter 8 for the inline mixer can inherently eliminate the offset.

In general the fastest pH control system with the largest reagent valve should be the first stage and the first line of defense to bear the brunt of an upset so that oscillations have a smaller period and can be effectively filtered out by larger downstream volumes per Equation 1-2a. The recovery time is faster and the amount of off-spec material is smaller for a fast system. It will be shown that the period of oscillation is proportional to the loop dead time and the integrated error is proportional to the loop dead time squared.



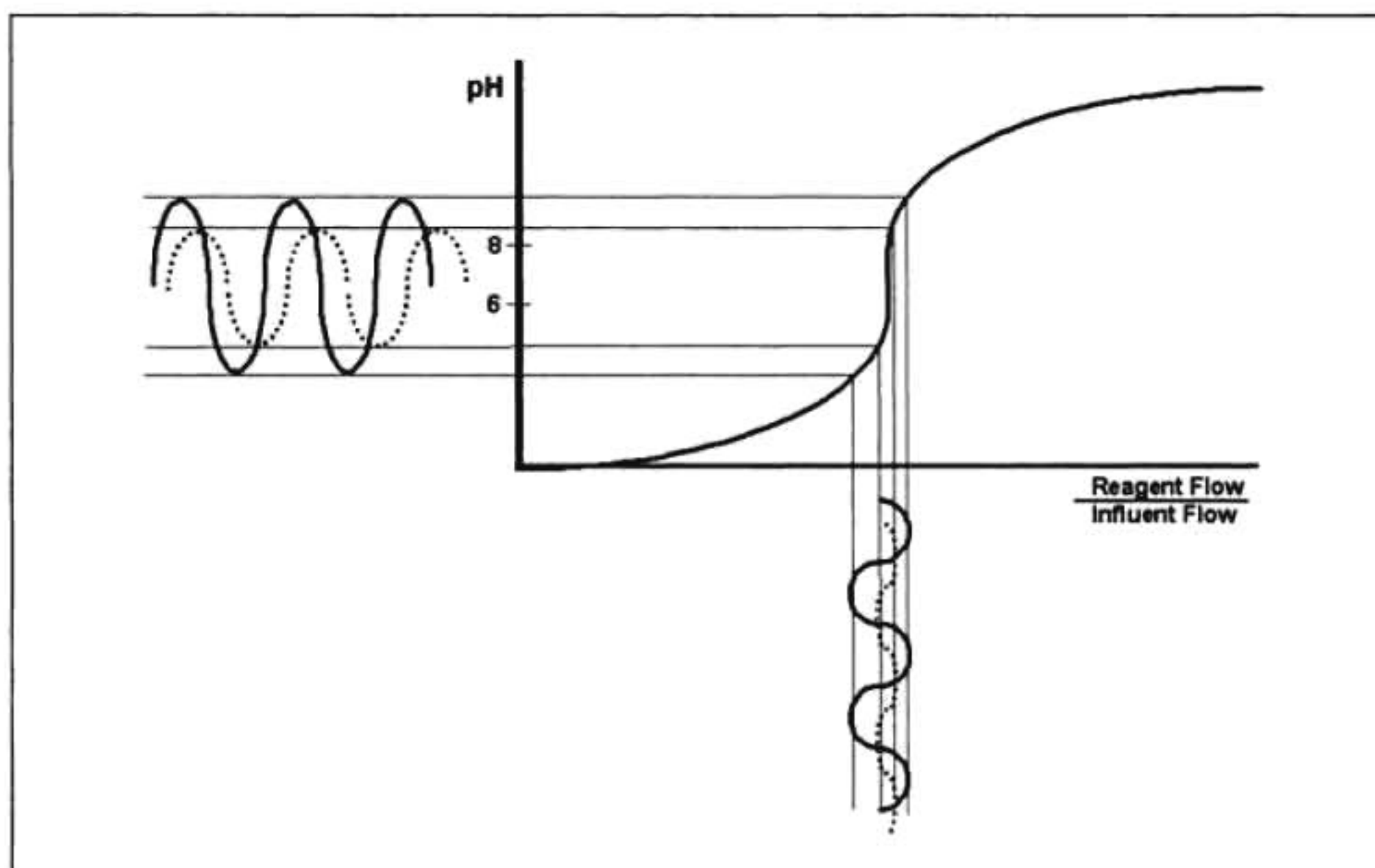


Figure 1-2a. Oscillations Should Be Translated between Axes of the Titration Curve



The average or filtered signal pH will not equal the actual pH downstream because of measurement errors and noise and the titration curve.

Another consideration is resonance of oscillations from two control loops in series. The first stage should have a total dead time from mixing and transportation delay that is at least five times faster than the next stage to minimize amplification of upsets from the resonance of in-phase oscillations. Mixing and transportation time delays are proportional to volume so this translates to a volume for the first stage that is at least five times smaller than the volume for the second stage. The chapters on mixing equipment and reagent piping will discuss the major design considerations to minimize dead time. A control loop may do more harm than good if the upset has a frequency that is close to its own frequency. Consequently, inline systems with pH controllers should not be put in series because they have similar delays and hence periods.



*The volume of each stage should differ by a factor of five to minimize resonance with the smallest volume first to minimize recovery time.*

A typical system design would use a static mixer with a transportation delay of 0.05 minutes for the first stage and a well-mixed vessel with a



mixing delay (turnover time) of 0.25 minutes and a minimum residence time of 5 minutes for the second stage.

While a tank for smoothing or blending requires minimal agitation, it is critical to realize that a vessel used for pH control must be well mixed with a residence time that is at least 20 times the turnover time. Anything that falls short of this is disastrous because it creates large volumes of off-spec material and slow oscillations that persist downstream.



**A poorly mixed tank should never be used for pH control but can be effectively used to attenuate oscillations from an upstream pH loop.**

For a vessel to be classified as well mixed, the height should be less than 150% of the diameter and an axial pattern agitator should be used to provide a ratio of residence time to mixing turnover time that is greater than 20:1. The turnover time should be less than one minute and baffles should be used to improve the mixing pattern. If conventional baffles are not permissible because of the area where polymers, particles, or microbes can accumulate, special draught tubes and contoured bottoms are used to prevent dead zones.

There is a super cheap alternative for pH control. The use of a large volume with an inline pH controller around a pump in its recirculation line will provide an incredibly smooth pH from the vessel discharge [Ref. 1.2]. The volume doesn't need to be particularly well mixed. Jet mixers may be sufficient. It mostly needs to be large so it could be some tank salvaged from the equipment graveyard. The performance is achieved by blending a high recirculation flow with a much smaller influent flow and smoothing out the fast concentration oscillations from an inline system with a large volume per Equation 1-2a. It is important that the inline system have a properly located and precise measurement and valve per Figure 1-2b. The drawbacks to this system is the extra time required to bring the whole volume to the proper operating point on start up or for a set point change and localized high concentrations of acids and bases in the recirculation line.

In theory, an incredibly precise valve and accurate signal characterization could enable pH control from any influent pH to any set point. Such a valve does not exist but the combination of the right valve and set point can go a long way to eliminating equipment and saving on reagent use.



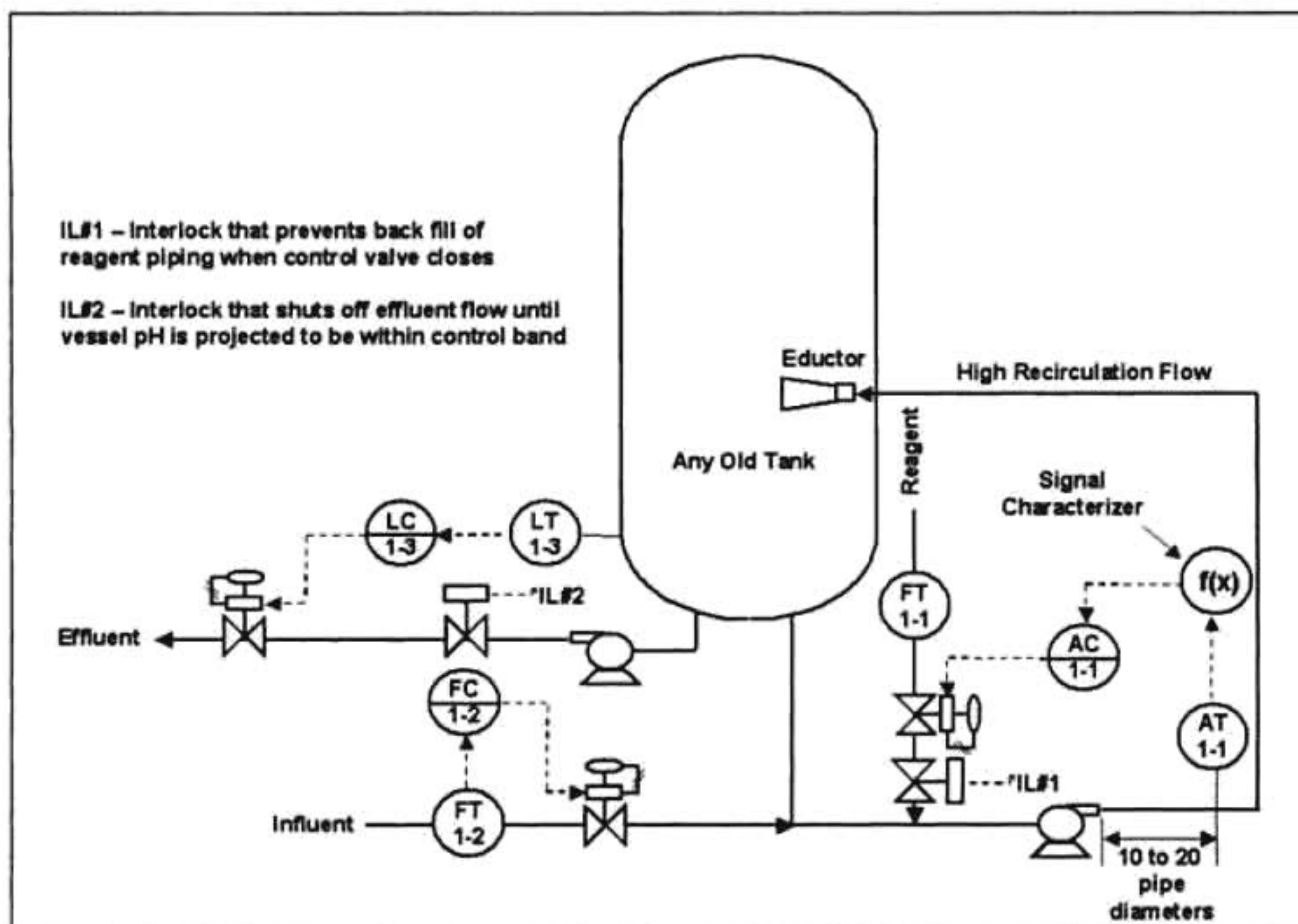


Figure 1-2b. A Really Cheap Way to Achieve Tight pH Control of Influent Upsets

### 1-3. Size Does Matter

The small valves typically used in pH control are more prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging. Here size does matter because most of these problems originate from extremely small Reynolds Numbers, clearances, and stem diameters [Ref. 1.4].



**Most of the problems with reagent throttling and injection stem from the extremely low flows required for pH control.**

For a  $C_v$  less than 0.01 or extremely viscous fluids, the valve may be operating in the laminar flow regime or in the region of transition from turbulent to laminar flow. Liquid flow moves from being approximately proportional to the square root of the pressure drop towards being proportional to the pressure drop as the flow goes from being fully turbulent to completely laminar. This can translate to an enormous sizing error. The result is often an oversized valve that rides the seat where the high seating friction causes excessive stick-slip. Even worse is operation in the transition region where the flow for a particular valve position has poor reproducibility because normally insignificant disturbances such as



microscopic changes in roughness or small vibrations can trigger a switch between turbulent and laminar flow and an erratic installed flow characteristic. Some reagents such as 98% sulfuric have a viscosity so high, starting the injection flow is like trying to get ketchup out of a bottle.



**Most reagent valves are oversized, which increases the amplitude of the oscillations from stick-slip.**



***Make sure valve sizing calculations take into account any transition to laminar flow and viscosity correction.***

If you also consider the possibility of a significant distortion of the inherent flow characteristic caused by machining tolerances that are an appreciable portion of the clearances for such tiny trim sizes, the scene is set up for an unknown and extreme nonlinearity. Tiny clearances can pose all sorts of problems because small particles and coatings cause plugging and sticking. The low flow velocities at the surface that is normally associated with laminar flow makes the likelihood of coating much greater.

Finally, tiny stems are likely to be bent from the normal handling both before and after installation. Slight deflections of the stem can cause huge amounts of stick-slip. What good is a control valve if you can't drop it or step on it?

Is the situation hopeless? Not if you go with a manufacturer who specializes in tighter machining tolerances, minimizing stick-slip, rugged stem guiding, and streamlined passages as shown in Figure 1-3a. Stay away from stems smaller than 3/8 inch and insist on getting response and flow test results. Use computer programs now available that properly deal with laminar flow and offer an installed characteristic curve for your piping and operating conditions. Even though the smart digital positioner may be larger and cost more than the valve, it is more important than ever that it be used and properly tuned for the small actuator volume. The challenge here is for packaged platforms that are going for low bid not to get cheap where it hurts [Ref. 1.4].



***Use precision machined industrial sliding stem (globe) valves with digital positioners tuned for the small actuator volumes to minimize stick-slip.***

If there is a tendency for plugging, pulse width modulation is a solution when there are sufficient back mixed volumes to attenuate the pulses. This



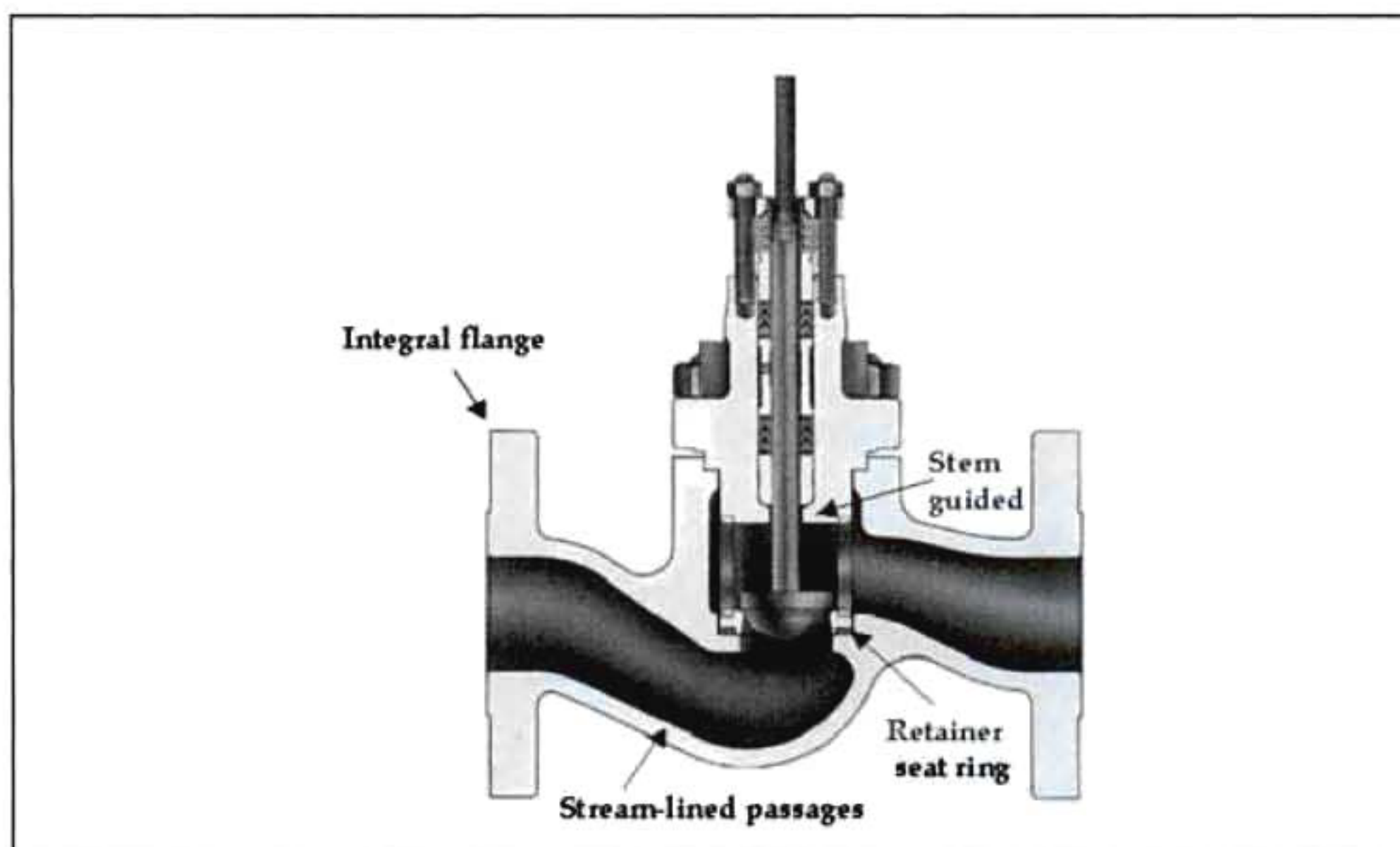


Figure 1-3a. Rugged Sliding Stem with Streamlined Passages for Corrosive Service

can also provide a linear flow characteristic and a flow large enough to be turbulent. The ratio of maximum to minimum pulse width establishes the rangeability. The maximum pulse width and hence cycle time determine the degree of variability that needs to be filtered and the additional dead time from the pulse off time. Now stroking time can be an issue because it is desirable to have the minimum pulse be as short as possible [Ref. 1.4].



*If the trim will plug, use pulse width modulation and set the ratio of the maximum to minimum pulse width to achieve the desired rangeability.*

Reagent dilution can eliminate these valve problems associated with low flow, but can introduce large reagent concentration disturbances and transportation delays if not done properly. Chapters 7 and 8 will discuss methods for precise reagent concentration control.

The installed characteristic of a throttled reagent valve is the inherent characteristic because the frictional loss in the piping is so small from the low flow. The pressure drop across the reagent valve is a large percentage of the system drop except for injectors with very tiny holes. In Chapter 8 on control system design, it will be shown that linear trims are best for vessels and equal percentage trims are best for static mixers when the pH controller directly manipulates a reagent valve instead of a reagent flow set point. As with any rule there are exceptions. The flow of acid and bases consumed by reactions can be so large that the installed characteristic of an equal percentage trim starts to resemble a linear characteristic and a linear trim starts to distort to a quick opening characteristic.



## 1-4. One Is the Loneliest Number

The reproducibility of a pH measurement on the steep part of a titration curve is rarely better than 0.2 pH if you include short- and long-term variability. If you move the set point to a flat part of the curve where noise is less, the reproducibility improves to 0.1 pH. Most of this error is caused by fluctuations in the reference electrode potential. If you use a properly designed flowing junction reference electrode, a reproducibility of 0.02 pH is possible. The 0.01 pH accuracy stated for electrodes is for the ideal laboratory environment and method and is a pipe dream for plant conditions. Technicians will ask you what you've been smoking if you tell them to keep a pH reading within 0.01 pH of a lab sample. Lab pH readings appear to be more consistent because the electrode is not inserted long enough for the coatings and changes in glass surface and reference junction potential to become an issue. For nasty streams, this short-term immersion is duplicated in the field by the use of automatically retractable pH electrodes that are sequenced to be inserted for a couple of minutes and then soaked or calibrated for 10 or more minutes.



The reproducibility of commonly used electrodes is about 0.2 and 0.1 pH for the steep and flat portions of a titration curve, respectively if the process is nice and the electrodes are properly selected, installed, and maintained.



*When the reproducibility must be better than 0.1 pH, use a pressurized flowing junction reference electrode with a reference fill solution that is compatible with the process.*



*For really nasty process fluids that seriously shorten the life expectancy of the electrode because of chemical attack, abrasion, dehydration, or coating, use an automatically retractable and sequenced assembly to minimize the electrode's process exposure and maximize its conditioning and calibration.*

The glass measurement electrode develops a potential in response to the activity of hydrogen ions at its glass surface. In theory, the hydrogen ion jumps from a hydronium ion in the aqueous solution to join up with a water molecule in the hydrated gel layer to form a hydronium ion in the glass surface as shown in Figure 1-4a [Ref. 1.5, 1.6, and 1.7]. The reproducibility of the measurement depends upon the condition of the hydrated gel layer, which is extremely thin. For solutions with low water concentrations, non-aqueous solvents, or high acid concentrations, the gel layer gets dehydrated and must be replenished by periodic soaking in water solution. Smart transmitters that measure the electrical resistance of



the measurement electrode can detect severe changes in the gel layer if the resistance is corrected for the effect of glass type and temperature.



The reproducibility of a measurement electrode depends on the condition of a thin gel layer that is easily disrupted by abrasion, dehydration, and chemical attack.

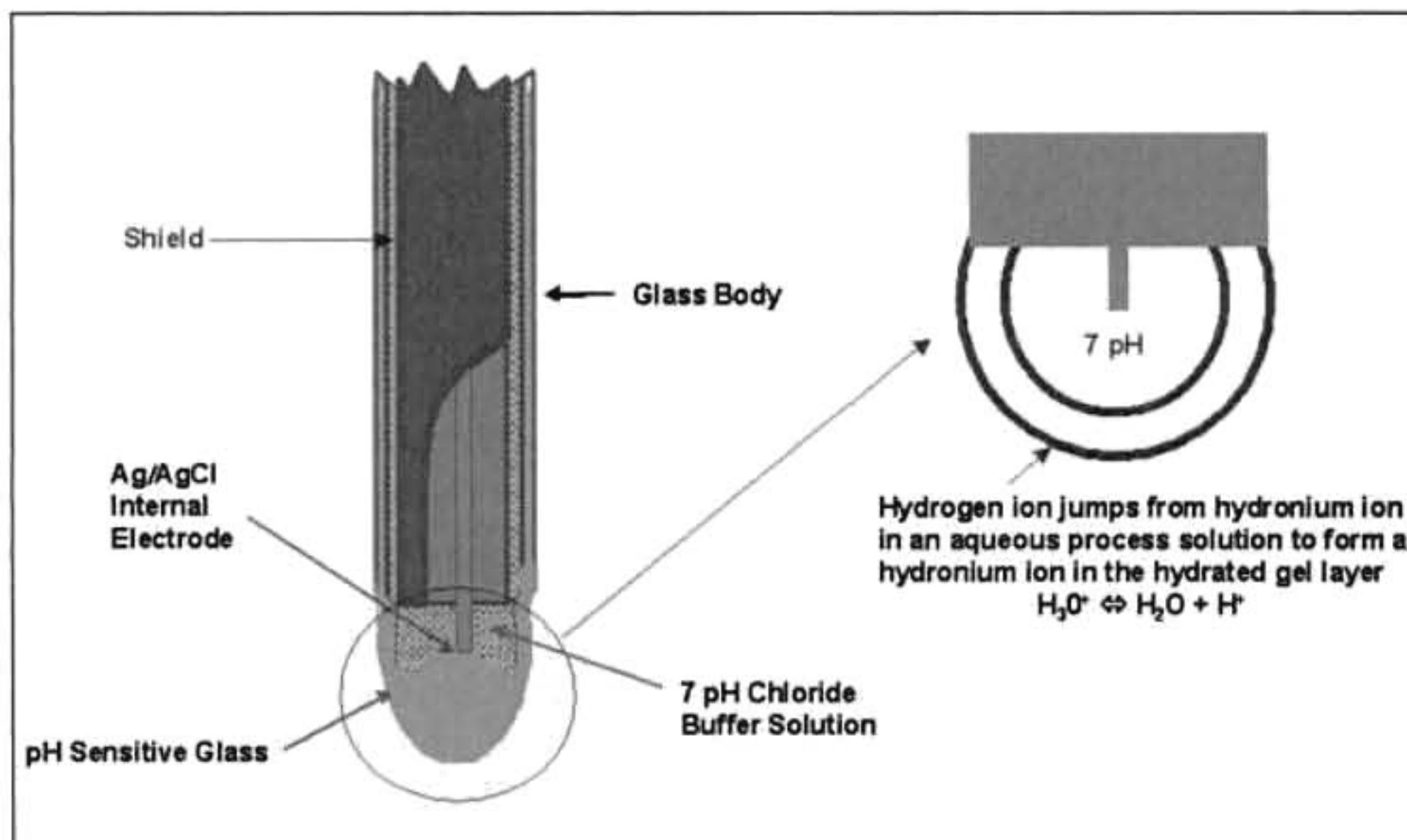


Figure 1-4a. The Measurement Electrode Depends on a Hydrated Gel Layer

High process temperatures shorten the electrode life per Figure 1-4b even for nice dilute aqueous solutions. High acid and base concentrations associated with operating below 2 pH or above 10 pH can chemically attack the glass surface and reduce its efficiency and life expectancy. Special glass formulations can help and, in general, the higher the electrical resistance of the glass the higher the chemical resistance. Thicker glass ("ruggedized") measurement electrodes are desirable from a stand-point of reducing breakage and resisting abrasion but the electrical resistance and the response time of these electrodes are larger and the active surface area of the dome shape is smaller. If these electrodes are used in an acidic stream that tends to dehydrate the gel layer, the problem is compounded. Low temperatures that exponentially increase the glass resistance also cause noisy erratic results for these higher resistance glasses. In general, no glass formulation provides an acceptable service life for hot ( $> 65^\circ\text{C}$ ) relatively concentrated sodium hydroxide solutions ( $> 10$  pH).



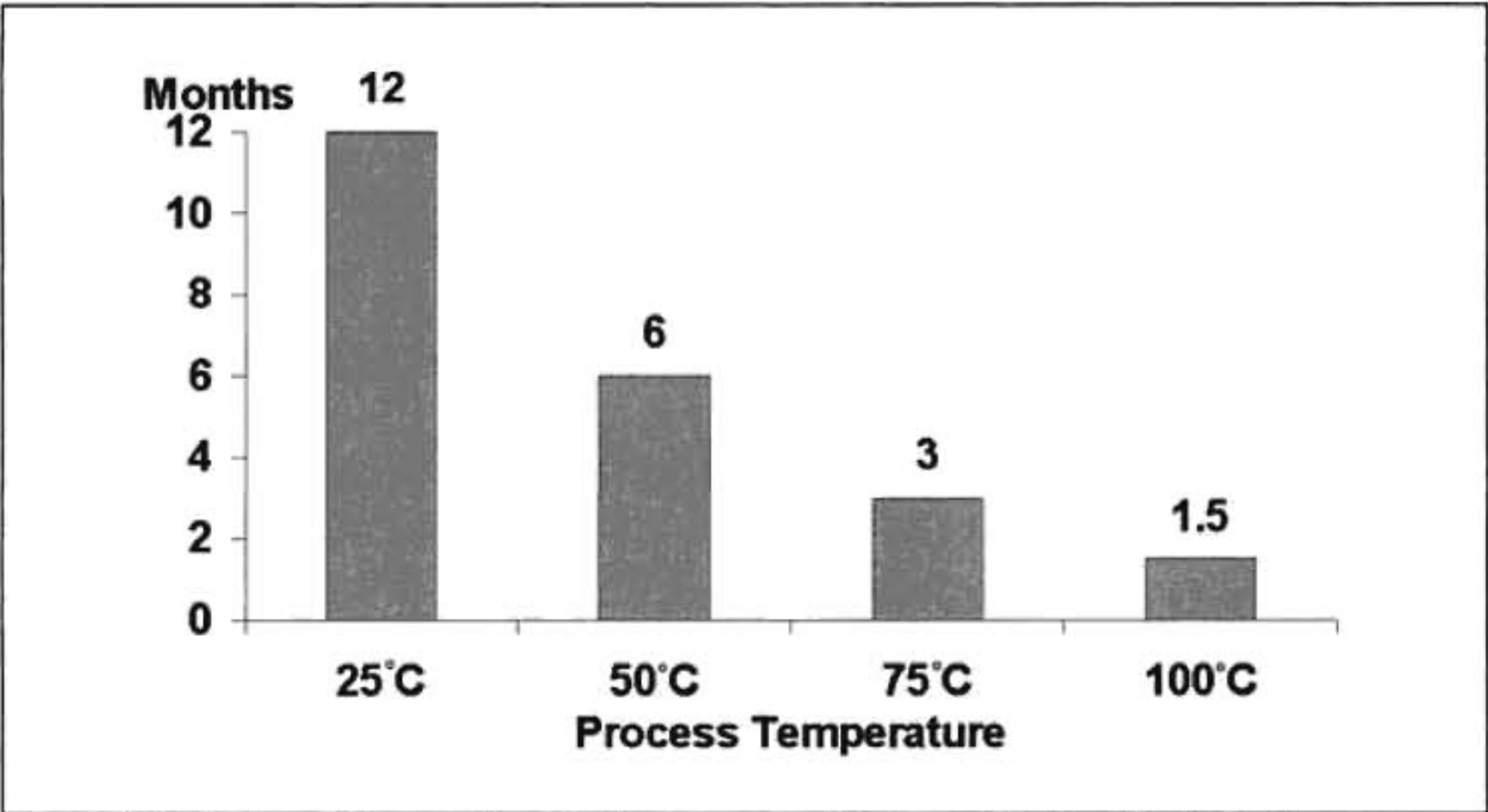


Figure 1-4b. Effect of Temperature on Measurement Electrode Life in a Nice Solution

The reference electrode is designed to provide a stable reference potential and provide an electrical path between the process and the internal electrode. To provide this electrical continuity, the reference fill must be in contact with the process, which figuratively and literally opens the reference electrode to all sorts of problems. The porous reference liquid junction shown in Figure 1-4c that allows the ions of the internal electrolyte to migrate and touch the process may allow process ions to migrate in the opposite direction and change the reference junction potential and eventually contaminate the internals. Pulsating pressures, high ionic strength solutions, and highly mobile ions accelerate the deterioration. A second much smaller internal junction is often used to protect the internal silver-silver chloride electrode. Particles and sticky fluids can also clog the junction. A large liquid junction surface area minimizes the clogging problem but increases the contamination problem. New solid references have large wood or plastic junctions with impregnated electrolyte ions to resist contamination. However, these junctions may be slow to reach an equilibrium potential. The most accurate and sure-proof alternative is a pressurized flowing junction reference. These are not popular in the U.S. because they require maintaining a pressurized reservoir to replenish the fill lost out through the junction. Also, a high junction flow can throw off measurements in beakers and contaminate a process. Smart transmitters can measure the junction resistance and detect clogging problems.

Most electrodes in service today are combination electrodes where the reference electrode is located in a ring around the glass measurement electrode. One manufacturer offers a combination electrode whose sleeve



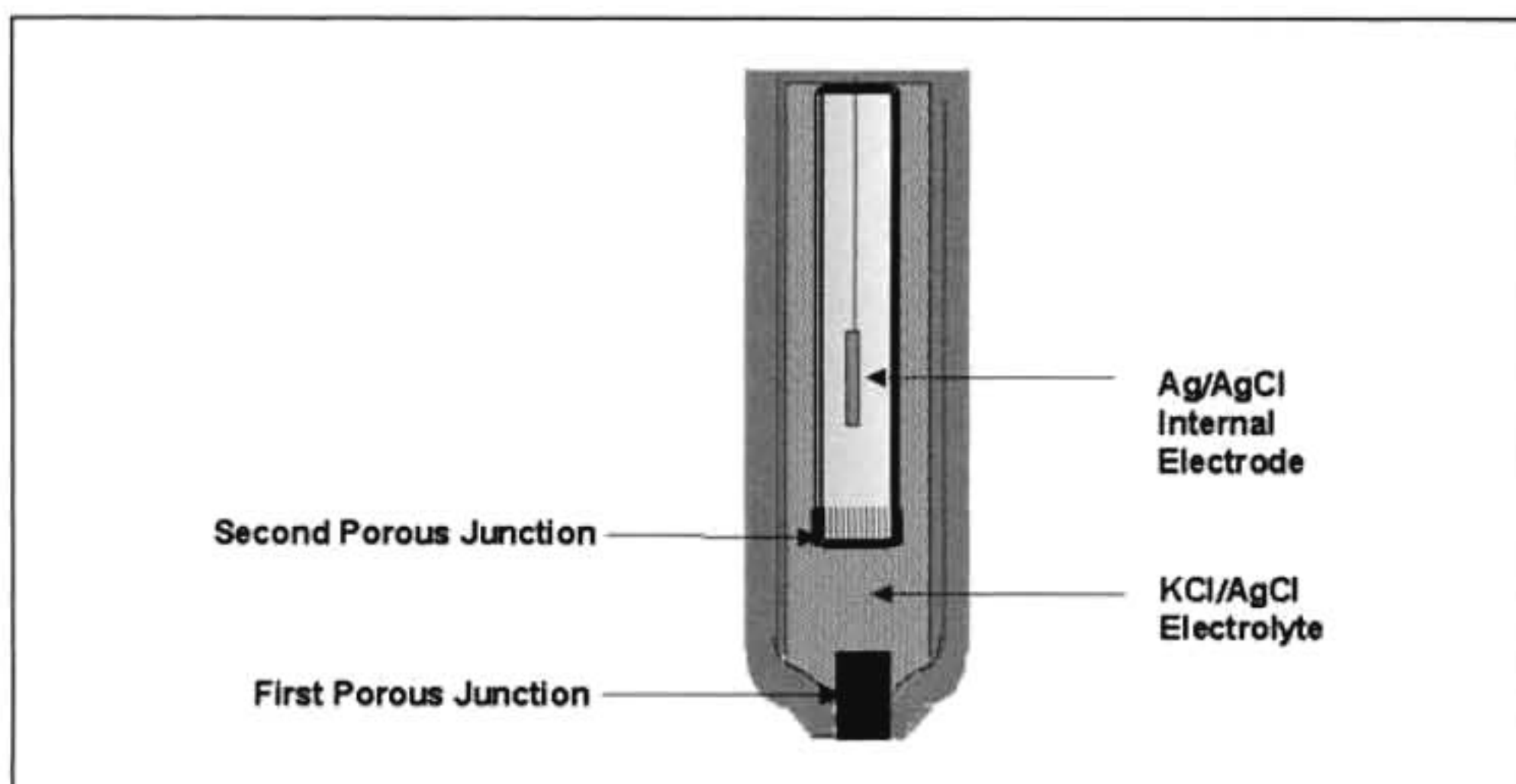


Figure 1-4c. The Reference Electrode Depends on a Porous Junction



The reproducibility of the reference electrode depends on its internal electrolyte ions quickly establishing and maintaining contact with the process but the process not clogging or migrating into the reference junction.



*The measurement electrode glass type and reference electrode junction and fill must be compatible with the process composition and temperature.*



*Smart Transmitters should be used to continually monitor resistances to infer the condition of the glass surface and the reference junction.*

Most pH systems are over calibrated while chasing sample results. If there is only one electrode, there is not much evidence to question the lab even though time, process temperature, and carbon dioxide content could explain the disagreement.

A second electrode will raise more questions than answers because the two electrodes will never agree because of concentration gradients, velocities, and the condition of the glass surface and reference junction. As seen in Figure 1-4d, what is high today may be low tomorrow although long-term trends may be observable, kind of like the stock market. Except for a sluggish or noisy response, it is difficult for the operator to establish which electrode to select so suspicion and prejudice prevail. Frequent



calibration adjustments often chase short-term transients and make the problem worse. The best results are often obtained by going to three electrodes and leaving them alone [Ref. 1.5].

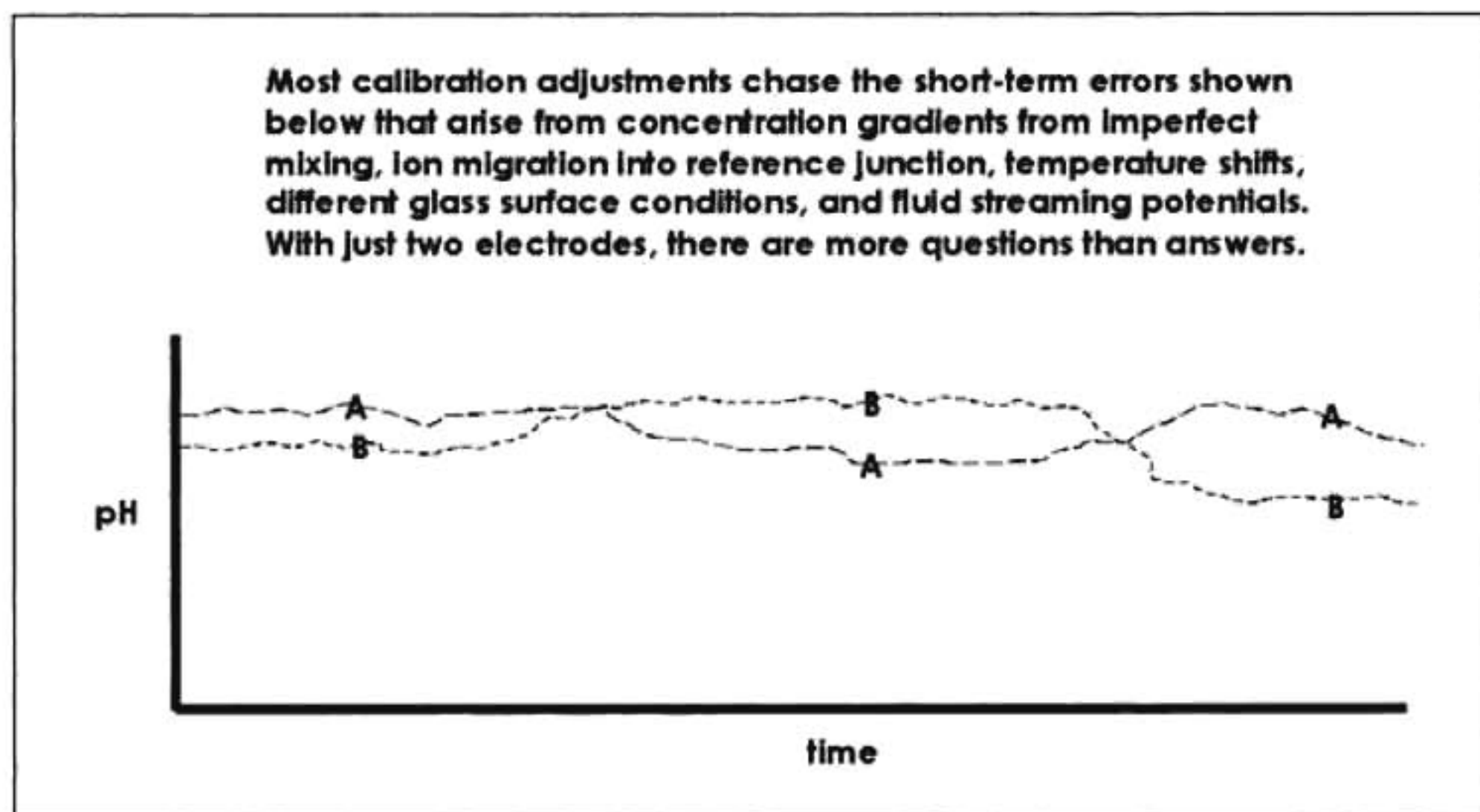


Figure 1-4d. What Is High Today May Be Low Tomorrow

The addition of a third electrode and the automatic selection of the middle signal will inherently ride out a spurious signal or failure of any type from one electrode. Often, engineers think they can design a better failure strategy but in fact, all other supposedly more sophisticated strategies for failure rejection have one or more modes of failure and can do more harm than good. The middle signal selection is often a standard function block that can be readily set up in most DCSs. Of course, if the process is truly nasty, you should not install three electrodes. You should go instead to automatically retractable and sequenced electrodes to minimize process exposure time.



*Middle signal selection will maximize the reliability and minimize the maintenance unless the process is so nasty it causes premature electrode failure.*

Finally, there is an opportunity to calculate pH online for the flat part of a titration curve if there are coriolis flowmeters to accurately measure the mass flow and density of two component mixtures or streams with sufficiently constant acid and base concentrations. An inferential measurement or pH estimator based on an online titration or charge balance model can become a third measurement that enables middle selection. In one application, it was found that the calculation was more accurate than the electrode readings because of the flatness of the titration curve. A single coriolis flowmeter on each of the influent and reagent



streams could be reliable and accurate enough to replace the use of electrodes altogether for the first stage of a neutralization system, which typically is on a very flat portion of the titration curve. Coriolis meters also offer the ability to display reagent usage, process efficiency, and automatically generated titration curves online. These opportunities will be explored in the chapter on control.



**Coriolis flowmeters can be used to replace pH electrodes and provide online displays of reagent usage, process efficiency, and titration curves.**

## 1-5. Acceleration and Stagnation

The approach to the neutral point looks like an accelerating response to the pH controller and is similar to what a temperature controller experiences for a runaway condition in an exothermic reactor. The tuning rule for such temperature controllers is to minimize reset action (maximize the reset time) and maximize rate action. Reset has no sense of direction and promotes overshoot. Rate anticipates where the process is headed by looking at the rate of change of the measurement and suppresses overshoot. However, rate will amplify noise and can generally only be used for pH control on back mixed volumes where there is a large enough process lag to provide a smooth and gradual response. For operating on the flat part of the curve, the controller gain should be increased to avoid stagnation. So for well mixed vessels, you can become famous by Friday if you simply decrease the reset setting and increase the rate setting [Ref. 1.8].



**The approach to the neutral point looks like a runaway response.**

For inline pH systems dominated by reagent and process transportation delays and spurious readings from concentration gradients, reset should be predominantly used to provide an averaging type of control and rate should be avoided [Ref. 1.8].



***Tune the pH controller with reset action (small reset times) for inline systems and with rate action (large rate times) for well-mixed vessels.***



If the titration curve is relatively fixed and known, it can be used to provide a feedforward signal. Generally this is simply flow feedforward where the reagent flow is ratioed to the influent flow and corrected by a feedback pH controller [Ref. 1.3]. It relies on a secondary reagent flow controller that receives a remote set point that is the flow ratio multiplied by the actual influent flow corrected by the pH controller output. If a flowmeter is not available for either the influent or reagent flow, an inferential flow measurement can be calculated from the installed valve characteristic and pressure drop.

Flow feedforward is generally helpful as long as you undercorrect for set points on the steep portion of the titration curve. It is particularly important for large feed flow changes and for systems with large dead times. The use of pH feedforward is generally not advisable if the influent measurement is on the extremes of the titration curve where the process conditions are harsh and the flatness of the titration curve increases the reagent error from measurement error. Deterioration in the glass surface and reference potential make the measurement error larger so there is a double hit in terms of the accuracy of the feedforward signal. pH feedforward works best when you are going from a steep part to a flat part of the titration curve. New adaptive control algorithms can automatically identify the feedforward gain and dynamics from feed set point changes.



Flow feedforward is generally helpful but can waste reagent by an over correction that is more likely when a set point is on the steep portion of the titration curve.



*Do not use pH feedforward control if the influent pH is on the extremes of the titration curve.*

For batch or continuous systems, a “head start” of the reagent valve position or reagent to influent ratio, can dramatically reduce the start-up time for low pH controller gains. The “head start” logic initializes the reagent valve or ratio to what was captured as the best value from the last run or batch. The initialization of the pH controller output is held until the actual pH reading has responded and is representative of the actual operating conditions on startup.



A “head start” of reagent valve position or flow ratio can dramatically reduce the start-up time for low pH controller gains.





*The initialization of the pH controller output on start-up should be held until a representative pH measurement is available for feedback control.*

There is a great tendency for pH systems to develop equal amplitude oscillations between the flat portions of the curve. People who use the ultimate oscillation method to tune a pH controller often choose a higher than actual ultimate gain because a wide range of gains create equal amplitude oscillations. Higher gains will tend to make the amplitude slightly larger but this is not perceptible and the amplitude never grows as with classic instability because the cycle is limited by the flat parts of the titration curve. The user needs to look for the start of damped oscillations to avoid confusion with the limit cycle [Ref. 1.8].



**A pH controller tends to cycle with equal amplitude oscillations.**



*Do not use the ultimate oscillation method for tuning pH controllers but instead find the gain that causes damped oscillations.*

For a fixed and known titration curve, an opportunity exists to linearize the process gain by signal characterization of the controlled variable [Ref. 1.2]. The X axis of the titration curve is scaled 0 to 100% of the operating range. Signal characterizer function blocks are then used to calculate the X axis (reagent demand) from the Y axis (pH) by entering pairs of data points. The controlled variable is now 0% to 100% reagent demand. This strategy works particularly well if the set point is on the steep part of the curve. It avoids the pH getting hung up on the flat part of the curve. It may do more harm than good if the set point is on the bend in a curve, and you must avoid at all costs getting on the steep part because it will slow down the response on the steep part. It is better in this case for the controller to see the acceleration and use rate action to kick the pH back to the flat part.



**Signal characterization of the controlled variable is a powerful tool for linearization if the set point is on the steep portion of a fixed titration curve but may be counter productive to prevent excursions into the steep region for set points on the bend in the curve.**



If a linear trim reagent valve is not available for vessel pH control, then signal characterization of the manipulated variable can reduce the nonlinearity introduced by the valve. In this case, the signal characterizer block is on the controller output.

For a variable or unknown titration curve, an adaptive controller that will find the changes in process gain can fill in the blanks. New algorithms have been developed that can identify the process dynamics for a set point change or by automatic injection of a short step into the controller output. The combination of adaptive control with signal characterization can be a powerful “one-two punch” to eliminate the nonlinearity.



*The combination of adaptive control with signal characterization can be a powerful “one-two punch” to eliminate nonlinearities.*

Figure 1-5a illustrates a myriad of advanced control techniques for a two-stage system where the first stage is a static mixer and the second stage is a well mixed tank. It shows the use of signal characterization, pH and flow feedforward, adaptive control, and real-time optimization of the stage 1 set point to minimize reagent usage.

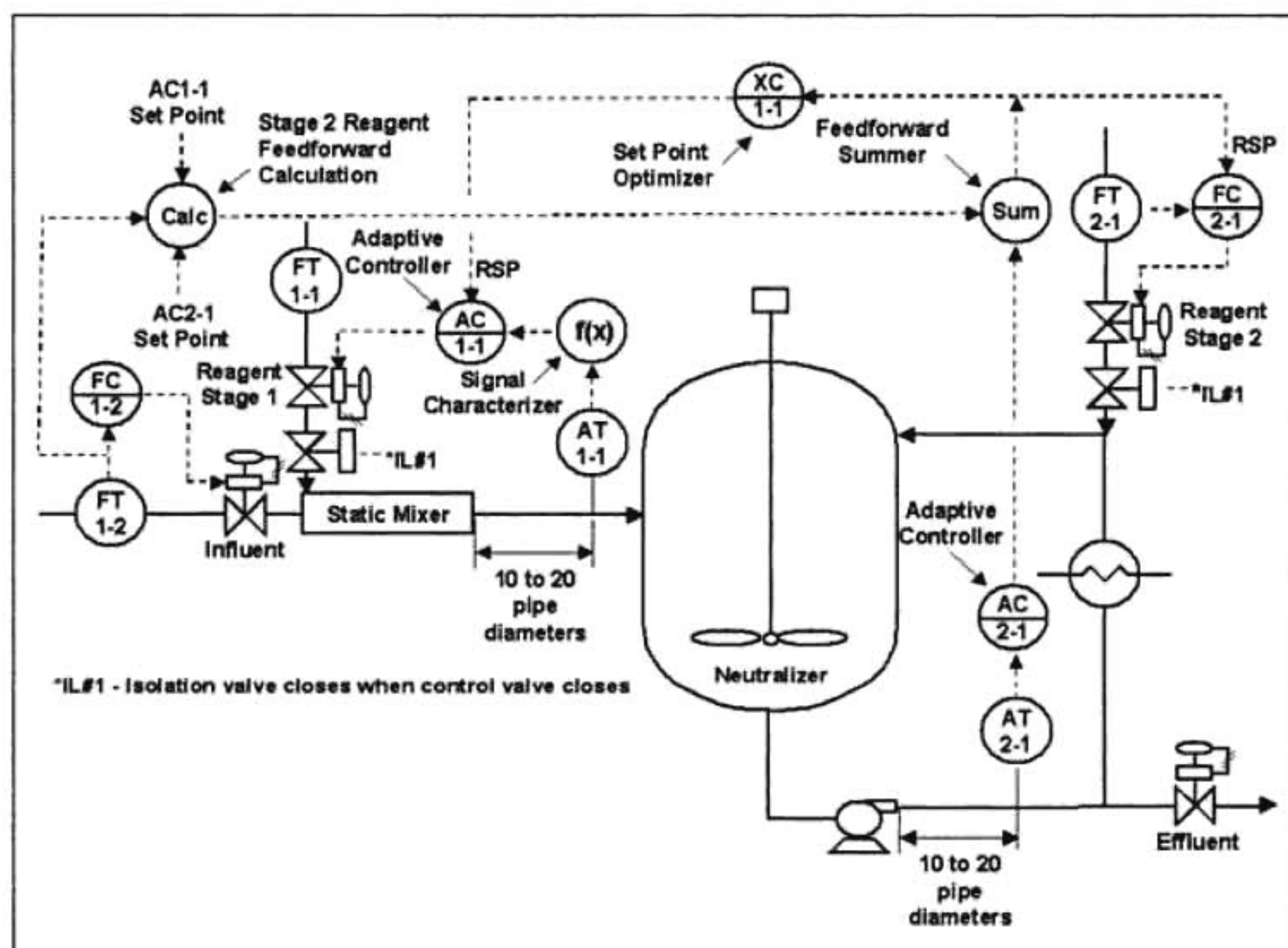


Figure 1-5a. Advanced Control Techniques to Minimize Reagent Usage



## 1-6. Life Is a Batch

All processes have a beginning and an end. A continuous process can be thought of as a long batch that can benefit from the automation of its start-up and shutdown by the use of sequencing techniques and standards developed for batch operations. One important distinction between batch and continuous is that during the reaction or formation of product, the vessel discharge flow is zero for batch operations. For batch reactors where the reagent is consumed or for fed batch operations where the reagent and feeds are simultaneous, the response is self-regulating and many of the design techniques developed for continuous control and optimization apply. For more traditional batch operation where the reagent and feeds are charged sequentially, the pH response is a ramp. This integrating response has profound implications as to controller tuning and strategies. It is more critical than ever to minimize the reset action (maximize reset time) and maximize rate action to prevent overshoot. If the pH goes past the end point, the only way it can be corrected is by use of split ranged of acid and base reagents. Often there is a dead band between the closing of one valve and the opening of the other valve to prevent cross neutralization. However, the combination of a dead band and an integrating response results in a continuous cycle even if there is no stick-slip. If you also consider that the split range point for the reagent valves is the point of greatest valve gain discontinuity and stick-slip, split ranged operation can significantly increase the cost of reagents and create excess salts. To prevent wasteful cross neutralization, reset is turned off or reagent addition is shutoff once the pH is within an acceptable control band.



If there is no consumption of reagent in a traditional sequential batch operation, the pH response is integrating and the pH loop will continuously oscillate across the split range point.

Most batch operations to date use mass flowmeters to charge a total mass of reagent specified by a recipe. The operator may then send a sample to the lab and make some manual trim adjustments. The use of an online pH measurement and one or more of the advanced batch control strategies listed in Table 1-6a can reduce batch cycle time and improve consistency. If the starting pH is on a relatively steep part of the curve, then a temperature corrected curve can be used to calculate the charge required based on the change in mass ratio on the X axis (item 1). However, if the pH at the start of the reagent addition is on extremes where the conditions are harsh and the reagent ratio error is large, it is best to use a recipe number that was updated by the actual reagent used in the last best batch



(item 2). A filtered and velocity limited rate of change of pH can be multiplied by the total time delay to provide a predicted pH that when compared to the desired end point can provide an anticipation needed to prevent overshoot (item 3). Pulse width and amplitude modulation of the pH controller output can mimic the titration method used in the lab (item 4). Finally, inline pH control of a high recirculation flow can provide a smooth transition to the end point if the localized high reagent concentrations do not trigger side reactions, damage cells or crystals, or corrode recirculation piping and nozzles (item 5). The inline pH control set point is remotely set by a batch pH controller with its reset turned off when the batch pH approaches the end point. What works best may be a combination of an initial charge just short of the end point based on items (1) and (2) and then a combination of items (3) and (4) or (5) to make a trim adjustment.

Table 1-6a. Advanced Batch pH Control Techniques

1.	Automatic calculation of charge from temperature corrected titration curve
2.	Automatic partial correction of charge based on last best batch
3.	Automatic end-point prediction and shutoff based on rate of change of pH
4.	Pulse width and amplitude modulation of a proportional-only controller output
5.	Cascade of batch pH to inline pH control of a high recirculation flow

1-7. Industrial Importance

In the food and beverage, chemical, petrochemical, pharmaceutical, power, pulp and paper, and textile industry, pH measurement and control is important for process efficiency and product quality, besides protection of the environment. Table 1-7a summarizes the importance of pH for various industrial applications. The number of pH loops in new plants will exponentially increase as bioprocesses move from the laboratory to plant production. The suppression of alien organisms and the yield of genetically engineered organisms are greatly dependent on tight pH measurement and control. The cost of a bad batch and contaminated equipment can be millions of dollars for high value-added pharmaceuticals [Ref. 1.9].



**Table 1-7a. The Importance of pH in the Process Industry**

<b>Application</b>	<b>Processes and Aspects Affected by pH</b>
Bacteriology	Microorganism growth and metabolism
Baking	Dough volume, texture, and color
Brewing	Yield of extract and sugar during mashing
Canning	Time and temperature for sterilization
Chemicals	Impurities and crystallization of salts
Cleaners	Effectiveness of removing paint and varnishes
Dyes	Yield and uniformity through intermediates
Electroplating	Nickel deposit hardness and brightness
Fermentation	Fermentation time and alien organism growth
Gelatin	Water absorption, solubility, and clarity
Pharmaceuticals	Effectiveness, stability, and body reaction
Pigments	Uniformity of composition in precipitation
Pulp and paper	Sizing, loading, coating, and foaming
Sewage	Digestion time, odors, and foaming
Sugar	Inversion of sugar and destruction of glucose
Textiles	Efficiency of most wet processes
Water treatment	Coagulation and softening processes

**1-8. The Real Deal**

Table 1-8a summarizes the Facts of Life from a decade of pH control start-ups that can be best described as a “Magical Mystery Tour” [Ref. 1.2].



**Table 1-8a. The Facts of Life**

1.	Instrumentation is frequently the source of disturbances for pH systems through reproducibility error, measurement noise, and valve stick-slip.
2.	Inline pH loops will oscillate regardless of controller tuning, if the set points are on the steep parts of titration curves.
3.	pH electrode submersion assemblies with unencapsulated terminations below the liquid surface will eventually have wet terminations.
4.	Reagent control valves that are not close-coupled to the injection point will cause reagent delivery delays long enough to reach early retirement.
5.	You need either a flowmeter or a seer to diagnose reagent delivery problems.
6.	Flow feedforward signals must be corrected by a pH feedback controller unless you like late night calls from operations.
7.	Transportation delays to pH electrodes in analyzer houses will exceed mixing time delays to such an extent that the increasing comfort of checking electrodes is offset by a decreasing comfort in checking trend recordings.
8.	Injection electrodes in recycle lines should be preferred to sample holder and submersion assemblies to reduce maintenance cost and coatings and improve response time, but not all injection electrodes are equal.
9.	Large poorly mixed tanks are fine if you don't have to control them. Use them upstream to reduce reagent consumption or downstream to filter out oscillations. If you can't make up your mind where to use them, put them downstream.
10.	Two measurements without an estimator will raise more questions than give answers.



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# **Chapter 2: The Chemistry**



## Chapter 2

### The Chemistry

#### 2-1. Nearly Normal

More than any other field, successful pH applications require good communication between the chemist, specialist, and plant engineer. Unfortunately, they all tend to speak different languages because what is normal in terms of units for one is not nearly normal for the other, and normality units, which are the most descriptive, are not normally used.

The units that chemists and engineering specialists most frequently use to quantify the concentration of acids and bases in a solution are molar, molal, and normality. The concentration unit that plant engineers commonly use is weight or mass fraction. However, since what is shown on process flow sheets and the specifications for control valves are reagent and influent flows, it is desirable to be able to convert from any of these concentration units to flow units. It will be shown in the remainder of the text how valuable it will be for control valve sizing and pH system analysis to have the ratio of reagent to influent flow as the abscissa of the titration curve.



**Chemists and specialists will provide data in concentration units that should be converted to influent flow conditions and reagent flow requirements.**

Molar units are predominately used by chemists making laboratory measurements because the calculation is based on a beaker volume. Molar concentration is the number of gram-moles per liter of solution. The number of moles is calculated by taking the weight of the pure acid or base and dividing it by its molecular weight expressed in the same weight units. The weight units used should be denoted with a dash in front of the word "moles" (i.e., lb-moles and gm-moles). Equations 2-1a and 2-1b show how to calculate gm-moles and then the concentration in molar units. It is important to remember in using these equations to convert all weight units to grams and all volume units to liters.

$$n = \frac{d * x * V}{M} \quad (2-1a)$$



$$c = \frac{n}{V} \quad (2-1b)$$

where:

- c = molar concentration of diluted acid or base (gm-moles per liter)
- d = density of solution (gm per liter)
- M = molecular weight of pure acid or base (gm per gm-mole)
- n = number of gm-moles of pure acid or base
- V = volume of solution (liters)
- x = weight fraction of pure acid or base in solution

Molal units are used predominately by engineers and scientists studying electrolytes because the concentration calculation is independent of density and, hence, temperature. Molal concentration is the number of gm-moles per 1000 gm of solvent. Equations 2-1c and 2-1d show how to convert between molal and molar concentrations. Note that as the acid or base weight fraction approaches one (the grams of solvent approaches zero), the molal concentration approaches infinity.

$$m = \frac{1000 * n}{d * (1 - x) * V} \quad (2-1c)$$

$$c = \frac{d * (1 - x) * m}{1000} \quad (2-1d)$$

where:

- c = molar concentration of diluted acid or base (gm-moles per liter)
- d = density of solution (gm per liter)
- m = molal concentration of diluted acid or base (gm-moles per kg solvent)
- n = number of gm-moles of pure acid or base
- V = volume of solution (liters)
- x = weight fraction of pure acid or base in solution

Normality units are normally used in pH simulations, which use charge-balance equations for acid and base ions. Normality concentration is the grams-ions of replaceable hydrogen or hydroxyl groups per liter of solution. A shorter notation of gram-equivalents per liter is frequently used. Equations 2-1e and 2-1f show how to convert between normality and molar units. Table 2-1a shows the normality versus weight percent for some common reagents. Note that normality is not proportional to weight percent for a given reagent because the density of the solution also changes.

$$N = \frac{z * d * x}{M} \quad (2-1e)$$



$$c = \frac{N}{z}$$

(2-1f)

where:

- d = density of solution (gm per liter)
- M = molecular weight of pure acid or base (gm per gm-mole)
- n = number of gm-moles of pure acid or base
- x = weight fraction of pure acid or base in solution
- z = number of replaceable hydrogen or hydroxyl ions per molecule of acid or base
- N = Normality (grams-ions of replaceable hydrogen or hydroxyl groups per liter)

Table 2-1a. The Normality of a Reagent Is Not Proportional to the Weight Percent

Reagent	Wt%	Normality
Hydrochloric acid (z = 1)	32	10.17
	38	12.35
Sulfuric acid (z = 2)	62.2	19.5
	77.7	27.2
	93.2	35.2
	98.0	36.0
Sodium hydroxide (z = 1)	10	2.75
	20	7.93
	50	19.1
Calcium hydroxide (z = 2)	5	1.36
	10	2.78
	15	4.3

As previously mentioned, it is desirable to use a ratio of reagent to influent flow for the abscissa of the titration curve for pH control system design. The method followed in this text will be to convert the concentration of the acid or base from the reagent, or influent streams in the effluent stream in molar, molal, and normality units to weight fraction via Equations 2-1a, 2-2a, or 2-3a (solve the equations for x).

It is necessary to eliminate mixing and residence time dynamics when using the titration curve since it is a steady-state plot. Toward this purpose, it helps to visualize the influent and reagent streams combining in a pipeline instead of a tank so that there is an immediate translation from a change in reagent or influent flow to a change in the weight fractions of the effluent stream. For pure (undiluted) acid or base reagent



and influent streams, the ratio of the reagent to influent flow is equal to the ratio of the weight fraction of the acid or base in the effluent stream. Normally, the concentration of the acid or base in the influent and reagent is not 100%, so the weight fraction of the acid or base in the individual influent and reagent streams is used to calculate the diluted stream flows needed for control valve sizing and feedforward calculations via Equations 2-1g and 2-1h. In using weight fractions, it is necessary to designate which stream is the source of the acid or base and which stream is the destination to form a mixture. To reduce confusion in Equations 2-1g through 2-1l, the subscript "rr" will designate the concentration of the acid or base reagent in the effluent stream; "re" will designate the concentration of the acid or base reagent in the effluent; "ii" will designate the concentration of the incoming acid or base in the influent stream; and "ie" will designate the concentration of the incoming acid or base in the effluent throughout the text. Since the influent flow is usually known before the effluent flow, Equation 2-1h is substituted for  $F_e$  in Equation 2-1g to yield Equation 2-1i for calculating the reagent flow. The desired flow ratio for the abscissa of the titration curve is the ratio of the diluted reagent to the diluted influent mass flow, which per Equation 2-1i is equal to the ratio of the reagent to influent weight fractions in the effluent multiplied by the inverse of the ratio of the reagent to influent weight fractions in the incoming streams. To convert from mass flow to volumetric flow, each mass flow must be divided by the diluted stream density in consistent units. Note that most reagent concentrations are given in weight percent and must be divided by 100 to get the weight fraction of the diluted reagent. If the initial sample volume is known, the abscissa is the volume of reagent titrated to reach the pH set point is specified, and the reagent concentration used in the laboratory and plant are equal, then Equation 2-1j can be used to calculate the volumetric reagent flow rate from a laboratory titration curve.

The chemist often doesn't like working with the high concentrations used in the plant because they are more hazardous and titration is more difficult since the drops required are much smaller. Since you don't normally have this luxury of a highly dilute reagent, you need to multiply by the ratio of the plant to lab weight fractions per Equation 2-1k. The volumetric flows can be converted to mass flows by multiplication by the respective stream's density. Equation 2-1l shows that effluent stream mass flow is equal to the sum of the influent and reagent stream mass flows.

$$F_r = \frac{x_{re}}{x_{rr}} * F_e \quad (2-1g)$$

$$F_i = \frac{x_{ie}}{x_{ii}} * F_e \quad (2-1h)$$



Solving 2-1h for  $F_e$  and substituting it into 2-1g:

$$F_r = \frac{x_{re} * x_{ii}}{x_{rr} * x_{ie}} * F_i \quad (2-1i)$$

$$Q_r = \frac{V_r}{V_i} * Q_i \quad (2-1j)$$

$$Q_r = \frac{V_r}{V_i} * Q_i * \frac{x'_{rr}}{x_{rr}} * \frac{\rho'_{rr}}{\rho_{rr}} \quad (2-1k)$$

$$F_e = F_r + F_i \quad (2-1l)$$

where:

- $F_e$  = effluent mass flow (kg per hr)
- $F_i$  = influent mass flow (kg per hr)
- $F_r$  = reagent mass flow (kg per hr)
- $\rho_{rr}$  = density of reagent acid or base in reagent stream in plant (kg per liter)
- $\rho'_{rr}$  = density of reagent acid or base in reagent stream in lab (kg per liter)
- $Q_i$  = influent volumetric flow (liters per min)
- $Q_r$  = reagent volumetric flow (liters per min)
- $V_i$  = influent sample volume used in laboratory (milliliters)
- $V_r$  = reagent volume titrated to reach pH set point in laboratory (milliliters)
- $x_{ie}$  = weight fraction of influent acid or base in effluent stream in plant
- $x_{ii}$  = weight fraction of influent acid or base in influent stream in plant
- $x_{re}$  = weight fraction of reagent acid or base in effluent stream in plant
- $x_{rr}$  = weight fraction of reagent acid or base in reagent stream in plant
- $x'_{rr}$  = weight fraction of reagent acid or base in reagent stream in lab



The calculations and curve from a chemist are often based on a reagent in a laboratory that is much more dilute than the reagent used in the plant.



## 2-2. Staying Active

Most discussions of pH measurement and control assume the activity of the hydrogen ion has not been diminished. Equations 2-2a through 2-2c show the relationship between hydrogen ion activity and concentration. Activity indicates an ion's ability to do the normal type of things that ions like to do, such as combining with other ions (association) and breaking free from compounds (dissociation). The ratio of the escaping tendency of the component in solution to that at a standard state is the official state sanctioned definition of ion activity. Equation 2-2c shows that the ion concentration multiplied by an activity coefficient is equal to the ion activity. Activities are dimensionless. The activity coefficient decreases from unity as the ion concentration increases from zero. In dilute solutions, the ions are far enough apart that the interaction between ions is negligible. Ion activity decreases as ion interaction increases. The change in activity is greater for ions with a large number of charges. As the concentration increases, the activity for some ions goes through a minimum and then increases due to ions grouping together. The activity of an ion also depends on the dielectric constant and temperature of the solvent and the concentration of the other ions in the solution. Table 2-2a lists the activity coefficients for some common ions in water for different ionic strengths.

The ionic strength of solutions can be approximated as the sum of one half of the product of the individual ion molal concentrations and their ion charge squared per Equation 2-2d from Reference 2.1. The ionic strength can then be substituted into Equation 2-2e to estimate its effect on the activity coefficient of the hydrogen (hydronium) ion. The hydrogen ion is less affected than other ions because it is more mobile. Most effluent streams in waste treatment are dilute enough that the activity coefficient for hydrogen can be considered equal to one. However this is not true for many reagent and some influent streams or for reactions where salts are formed. For highly concentrated streams, the pH becomes effectively a function of water content. In other words as the salt concentration goes up and the water concentration goes down, the pH will increase even though the concentration of acids or bases has not changed. Figure 2-2a shows how the pH increases with the concentration of sodium chloride.

$$a_H = 10^{-pH} \quad (2-2a)$$

$$pH = -\log(a_H) \quad (2-2b)$$

$$a_H = \gamma_H * c_H \quad (2-2c)$$



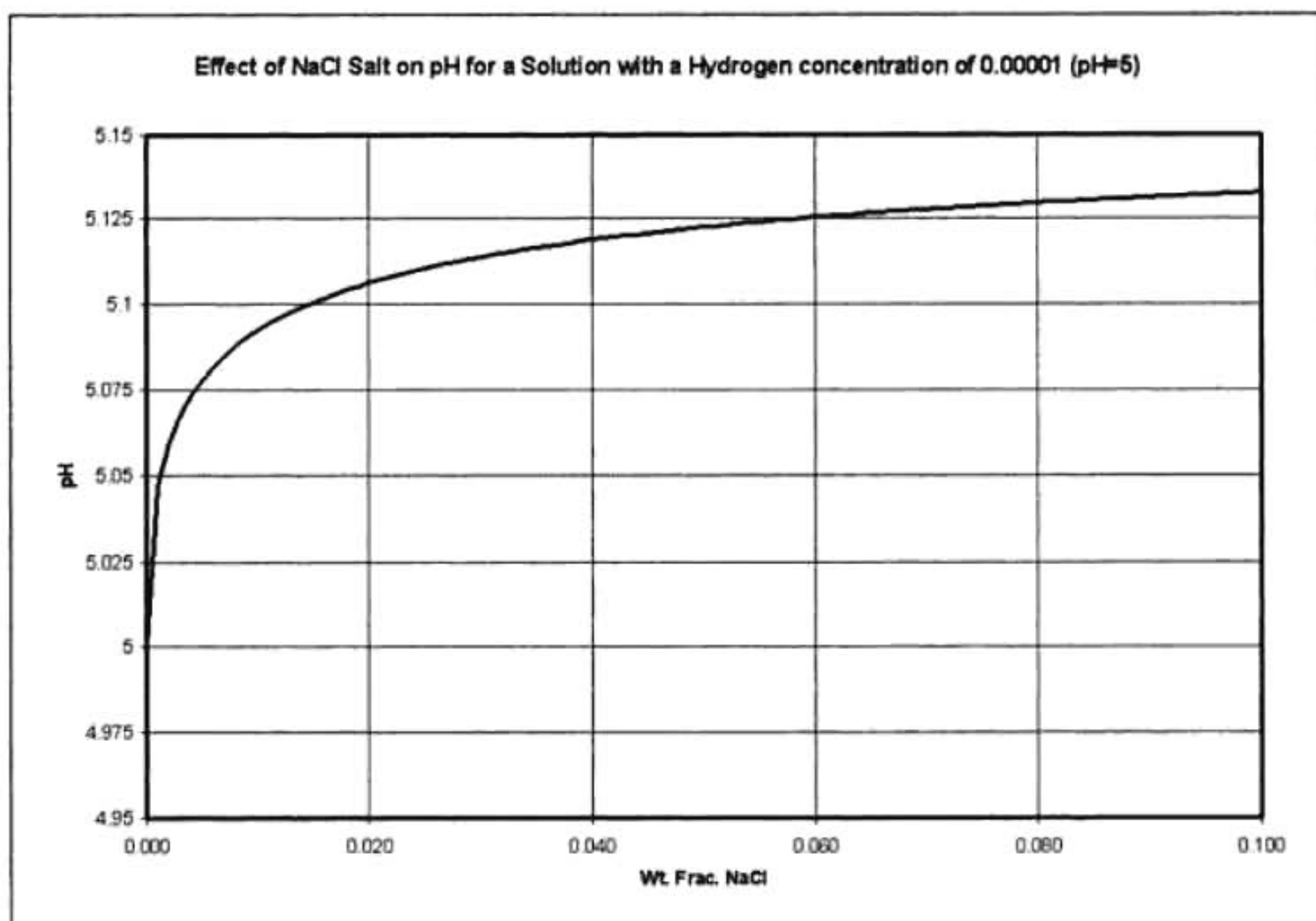


Figure 2-2a. Effect of Salt Concentration on pH

$$I = 0.5 * \sum_{i=1}^n (m_i * Z_i^2) \quad (2-2d)$$

$$\log \gamma_H = \frac{-0.5 * I^{0.5}}{1 + 3 * I^{0.5}} \quad (2-2e)$$

where:

- $a_H$  = activity of hydrogen (hydronium) ions (gm-moles per liter)
- $c_H$  = concentration of hydrogen ions (gm-moles per liter)
- $\gamma_H$  = activity coefficient for hydrogen ion (1 for dilute solutions)
- $m_i$  = molal concentration of salt ion  $i$  (gm-moles per kg of solvent)
- pH = negative base 10 power of hydrogen ions
- $I$  = ionic strength of stream at 25°C
- $Z_i$  = charge or valence of ion  $i$

Equation 2-2a shows the definition of pH in terms of hydrogen ion activity instead of concentration. A pH measurement is a relative rather than an absolute indicator of hydrogen ion activity because the measurement is referenced to a measurement with a hydrogen electrode in a water solution (see Chapter 4) that is not corrected for temperature and the activity of a single ion is difficult to verify in practice. Also, the pH measurement is in general not an indicator of hydrogen ion activity for



**Table 2-2a. The Activity Coefficient Depends on the Solvent, Temperature, Ion Size, Ion Valence, and the Ionic Strength of the Solution**

Ion Type	Ion Size (Angstroms)	$Z_i$ - Ion Valence (charge)	I - Ionic Strength in Water at 25°C			
			0.005	0.010	0.050	0.100
Hydronium	9	1	0.933	0.914	0.860	0.830
Lithium	6	1	0.929	0.907	0.835	0.800
Sodium	4.5	1	0.928	0.902	0.820	0.775
Hydroxyl	3.5	1	0.926	0.900	0.810	0.760
Potassium	3	1	0.925	0.899	0.805	0.755
Ammonium	2.5	1	0.924	0.898	0.800	0.750
Magnesium	8	2	0.755	0.690	0.520	0.450
Calcium	6	2	0.749	0.675	0.485	0.405
Carbonate	4.5	2	0.741	0.663	0.450	0.360
Sulfate	4	2	0.740	0.660	0.445	0.355
Phosphate	4	3	0.510	0.405	0.180	0.115

pure acids or for solvents other than water. Of greater importance is that a properly designed, installed, and maintained pH measurement with a consistent reference potential and glass gel layer can provide a reproducible experimental value. For a more complete discussion of the limitations of the pH measurement scale, the reader is directed to Reference 2.2.



An increase in salt concentration or decrease in water content will increase the solution pH even though the acid and base concentration is constant.

### 2-3. Free Dissociation

An acid is a molecule that yields a hydrogen ion when it dissociates (breaks apart into its component ions) as shown in Equation 2-3a and a base is a molecule that yields a hydroxyl ion when it dissociates as shown in Equation 2-3b. Water acts as both an acid and a base because it yields both a hydrogen ion and hydroxyl ion upon dissociation as shown in Equation 2-3c. Neutralization is the association of the hydrogen and hydroxyl ions to form water; it is designated by the reverse arrow in Equation 2-3c. Forward and reverse arrows in these equations show that ion association as well as dissociation occurs to maintain equilibrium

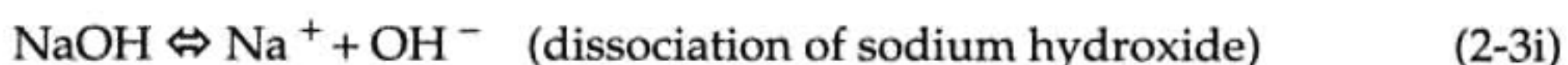
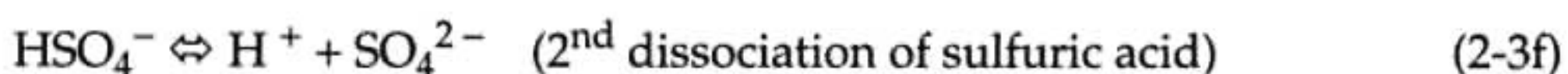
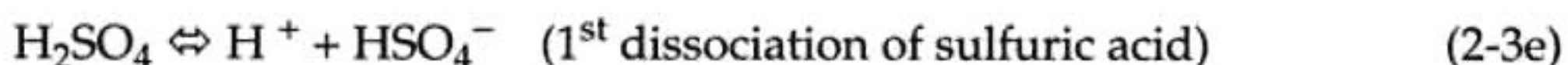
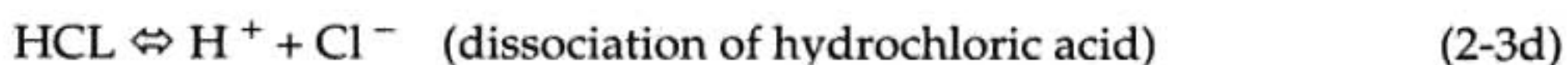
between the concentrations of the species on both sides of the equation. These acid and base definitions were developed based on aqueous (water) solutions. A more general definition of an acid as a proton donor and a base as a proton acceptor is needed for non-aqueous solutions. Since the visualization of these definitions is more difficult and data on non-aqueous pH measurement is scarce, these definitions will not be explored further. The practical problems with non-aqueous pH measurements will be discussed in Chapter 4. For more information on the proton donor and acceptor definitions, consult References 2.2, 2.3, and 2.8.



where:

- HA = acid molecule
- BOH = base molecule
- H<sub>2</sub>O = water molecule
- A<sup>-</sup> = negative ion from dissociation of acid
- B<sup>+</sup> = positive ion from dissociation of base
- H<sup>+</sup> = hydrogen ion (proton)
- OH<sup>-</sup> = hydroxyl ion

The dissociation of some common acid and base reagents is detailed in Equations (2-3d) through (2-3i). Note that sulfuric acid and calcium hydroxide dissociate twice and yield ions with a double charge.



Dissociation constants are used to define the relationship between the activities of the components in equilibrium with each other. They also provide a measure of the strength of the acid or base. In most applications, the stream concentration will be assumed to be dilute enough so that the



charge balance equations that utilize these dissociation constants will be simplified by the omission of activity coefficients. This assumption is usually valid for effluent streams, which are the streams of greatest interest in pH control loop performance analysis. The dissociation constant "K" typically falls numerically in the same range as the hydrogen ion concentration so that it is convenient to express it as a negative base ten logarithm like pH where the small p designates the power function, as defined in Equation 2-3j. It is helpful to convert each  $pK_b$  to a  $pK_a$  via Equation 2-3l because the effect of the acid or base concentration on the flattening of the titration curve and process temperature on the solution pH is greatest when the pH is at the  $pK_a$ .

$$pK_a = -\log K_a \quad (2-3j)$$

$$pK_b = -\log K_b \quad (2-3k)$$

$$pK_a = pK_w - pK_b \quad (2-3l)$$

where:

$pK_a$  = negative base 10 logarithmic acid dissociation constant

$pK_b$  = negative base 10 logarithmic base dissociation constant

$pK_w$  = negative base 10 logarithmic water dissociation constant

Equations 2-3r through 2-3w show the relationship between the species concentrations and dissociation constant for the dissociation of the common reagents shown in Equations 2-3d through 2-3i. Square brackets around each species denote that the quantity is a concentration in normality units. The numerator is the product of the ion concentrations while the denominator is the unionized acid or base concentration. The double subscript is used to designate the source and order of dissociation. A small "a" subscript designates the source is an acid and a small "b" subscript designates the source is a base. Frequently in references the small "a" and "b" subscripts are omitted. All such dissociation constants are for the hydrogen ion even though the source may be a base. Table 2-3a lists the  $pK_a$  for some acids and bases at 25°C in a water solution of zero ionic strength ( $pK_w = 14$ ). For bases, older references give a  $pK_b$  that must be converted to a  $pK_a$  for charge balance models and pH system analysis. The molecular weight is shown in the tables because it is used in molar, molal, and normality concentration calculations. For a more complete listing of dissociation constants, the reader is directed to References 2.4, 2.5, and 2.7.

It is important to realize that dissociation constants vary with temperature and hence the pH of the solution varies with temperature. A common misconception is that the temperature compensator in a pH measurement circuit corrects for this variation. Such compensators correct for the

change in millivolts per pH unit relationship for the glass electrode per the Nernst Equation. Smart transmitters have added the ability to specify a process pH versus temperature relationship. Fieldbus-based control systems have signal characterizers to calculate the correction to the set point or measurement.

The effect on temperature is greatest for pH values near a  $pK_a$  or a  $pK_w$ . Unfortunately, the data on the effect of temperature on a  $pK_a$  or  $pK_b$  is sketchy. In the absence of data, the change in  $pK_w$  with temperature, which ranges from a -0.01 to -0.03 per  $^{\circ}\text{C}$  as seen in Table 2-3b, can be used to estimate the variation in the  $pK_a$  above 7 pH with temperature. For strong acids and bases, the  $pK_a$  dissociation constants are by definition off scale and the change in the  $pK_w$  with temperature dominates. Figure 2-3a shows how the effect of the changes in the water dissociation constant with temperature on a strong acid and strong base solution is zero below 7 pH and reaches a maximum around 10 pH.

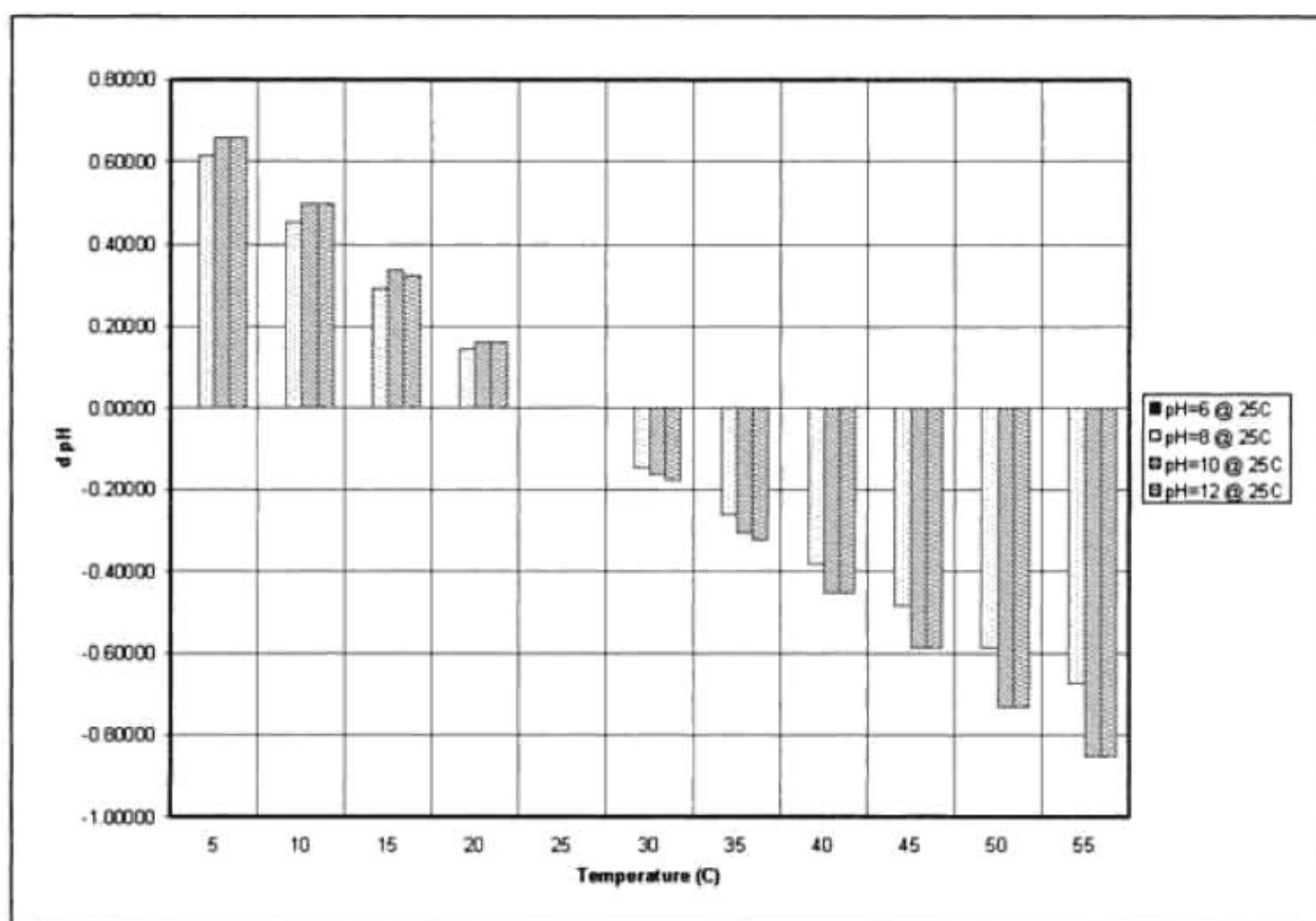


Figure 2-3a. Effect of Temperature on a Strong Acid and Base Solution

The acid or base strength increases as its  $pK_a$  or  $pK_b$  decreases. A  $pK_a$  or  $pK_b$  less than zero means that the product of the ion activities is greater than the activity of the source molecule. Such acids and bases are called "strong" since they are essentially completely dissociated in the 0 to 14 pH range. Correspondingly, acids with a  $pK_a$  or  $pK_b$  greater than one are called "weak." The relative weakness increases as the  $pK_a$  or  $pK_b$



increases. Note that the first dissociation constant of sulfuric acid classifies it as a “strong” acid while the second classifies it as a “weak” acid. In fact, sulfuric acid behaves like a mixture of “strong” and “weak” acid. When the pH equals the  $pK_a$ , the negative acid ion activity is equal to the acid molecule activity. The dissociation is at the midpoint. This midpoint can be spotted on the titration curve if the dissociation constants are not too close together and can be used as a flag for identifying the dissociation constants from laboratory titration curves for signal characterization and control system simulation programs. This technique will be discussed in greater detail in Chapters 3 and 7.



The  $pK_b$  for a base should be converted to a  $pK_a$  since the effect of ion activity and solution temperature is best seen when the pH approaches a  $pK_a$ .

Table 2-3a.  $pK_a$  for Dilute Aqueous Solutions of Acids and Bases at 25°C [Ref. 2.3 and 2.7]

Acid or Base	$pK_{a1}$	$pK_{a2}$	Molecular Weight
Acetic acid	4.76	—	60.05
Acrylic acid	4.26	—	72.06
Ammonium	9.24	—	18.04
Calcium hydroxide	12.80*	12.67	74.09
Carbon dioxide	6.35	10.33	44.01
Formic acid	3.75	—	46.03
Fumaric acid	3.10	4.60	116.1
Glutaric acid	3.77	6.08	132.12
Hydrogen chloride	-6.2	—	36.46
Hydrogen cyanate	3.46	—	43.03
Hydrogen cyanide	9.21	—	27.06
Hydrogen fluoride	3.17	—	20.01
Hydrogen iodide	-8.26	—	127.92
Hydrogen peroxide	11.64	—	34.02
Hydrogen sulfide	6.97	12.9*	34.08
Lactic acid	3.86	—	90.08
Magnesium hydroxide	11.41	—	58.33
Maleic acid	1.91	6.33	116.1
Nitric acid	1.44*	—	63.02
Phosphorous acid	2.00	6.40	82.00
Phthalic acid	2.95	5.41	166.1
Sodium hydroxide	14.67	—	40.01
Sorbic acid	4.77	—	112.1
Sulfuric acid	-3.0*	1.99	98.08
Uric acid	5.40	5.53	168.11
* - present value is disputed and should be adjusted for application per lab data			

Table 2-3b.  $pK_w$  for Dilute Aqueous Solutions as a Function of Temperature [Ref. 2.4 and 2.8]

Temperature (°C)	$pK_w$
0	14.94
5	14.73
10	14.54
15	14.35
20	14.17
25	14.00
30	13.83
35	13.68
40	13.54
45	13.40
50	13.28
75	12.71

The dissociation constants given in the literature are based on concentrations as shown in Equation 2-3m whereas in reality they should be based on activities as detailed in Equation 2-3n, which leads to the correction factors shown in Equations 2-3o and 2-3p.

$$K_a = \frac{[H^+] * [A^-]}{[HA]} \text{ (concentration based acid dissociation constant) (2-3m)}$$

$$K'_a = \frac{\gamma_H * [H^+] * \gamma_A * [A^-]}{\gamma_{HA} * [HA]} \text{ (activity based acid dissociation constant) (2-3n)}$$

$$K'_a = \frac{[H^+] * [A^-]}{[HA]} * \frac{\gamma_H * \gamma_A}{\gamma_{HA}} \text{ (activity based acid dissociation constant) (2-3o)}$$

$$pK'_a = \log K_a - \log \gamma_H - \log \gamma_A + \log \gamma_{HA} \text{ (2-3p)}$$

For relatively dilute solutions  $\log \gamma_H = \log \gamma_A$ ,  $\log \gamma_{HA} = 0$ , and  $\gamma_H$  can be approximated by the Debye-Huckel equation per Reference 2.5, which yields Equation 2-3q for the correction of a  $pK_a$  for the changes in ion activity. Sophisticated electrolytes modeling programs take into account ion activity. In reality, the activity coefficients are not known accurately for concentrated or multi-component solutions due to complex ion interactions and the user ends up tweaking the coefficients to match plant data.



$$pK'_a = pK_a - \frac{0.5 * m^{0.5}}{1 + m^{0.5}} \quad (2-3q)$$

$$K_a = \frac{[H^+] * [Cl^-]}{[HCl]} \text{ (dissociation constant for hydrochloric acid)} \quad (2-3r)$$

$$K_{a1} = \frac{[H^+] * [HSO_4^-]}{[H_2SO_4]} \text{ (1st dissociation constant for sulfuric acid)} \quad (2-3s)$$

$$K_{a2} = \frac{[H^+] * [SO_4^{2-}]}{[HSO_4^-]} \text{ (2nd dissociation constant for sulfuric acid)} \quad (2-3t)$$

$$K_{b1} = \frac{[OH^-] * [CaOH^+]}{[CaOH_2]} \text{ (1st dissociation constant for calcium hydroxide)} \quad (2-3u)$$

$$K_{b2} = \frac{[OH^-] * [Ca^{2+}]}{[CaOH^+]} \text{ (2nd dissociation constant for calcium hydroxide)} \quad (2-3v)$$

$$K_{b1} = \frac{[OH^-] * [Na^+]}{[NaOH]} \text{ (dissociation constant for sodium hydroxide)} \quad (2-3w)$$

$$K_w = [H^+] * [OH^-] \text{ (dissociation constant for water)} \quad (2-3x)$$

## 2-4. A Question of Balance

While mass, energy, and component balances are common place in simulation software, the charge balance that enables the calculation of pH is rarely employed even though the implementation is rather straightforward and the results very useful for generating titration curves for pH signal characterization, control valve sizing, and pH system analysis. While there is no direct solution of the charge balance for a complex mixture, an interval halving search for the pH that gives a zero net charge is fast, efficient, and fool proof. It has been found in practice that the effect of changes in ion activity can be included by the adjustment of the acid dissociation constants per Reference 2.6. Special-purpose electrolyte modeling programs can be used to provide estimates of the activity coefficients but some tweaking of the dissociation coefficients is inevitable.



A charge balance with its  $pK_a$  and  $pK_w$  coefficients adjusted for activity and temperature effects is a powerful tool for generating titration curves.

Since solutions are neutral, the existence of just one type of ion in solution is not possible. Thus, pH measurement cannot be stated to be a measurement of just the hydrogen ion. In water solutions, hydrogen ions will be accompanied by hydroxyl ions per the ionic product shown in Equation 2-3x. If no other ions are in the solution, charge neutrality demands that the hydrogen ion concentration equal the hydroxyl ion concentration. If other ions are in solution, the sum of each ion concentration multiplied by its charge (normality) must equal zero. This is fortunate because it permits the use of an interval-halving search method to iteratively search for the pH for a given set of ion concentrations that makes the charge balance zero. The excess charge is calculated for the pH guess at the midpoint of the pH search interval. If the excess charge is negative, the lower pH search limit is increased to the midpoint pH. If the excess is positive, the upper pH search limit is decreased to the midpoint pH. This interval halving continues until the interval is less than a specified allowable error. If the pH and concentrations of all but one acid or base in a solution are known, the unknown acid or base concentration can be solved for directly from the charge balance equation.

The charge balance equation is set up by summing the concentration in normality units of all the ions in solution and setting the sum equal to zero. The acid or base concentrations and not the ion concentrations are generally given. A strong acid or base is completely ionized so that the ion concentration is equal to the acid or base concentration. A weak acid or base is only partially ionized. The concentration of the ions can be calculated from the relationships for the dissociation constants and combined in an expression based on the acid or base concentration. Equations 2-4a through 2-4h show the expressions for single, double and triple dissociations, respectively, of a weak acid or base. For the derivations of the expressions for single and double dissociations, the reader is directed to Reference 2.7. A derivation of the expression for the third dissociation can be obtained by extending the same method. Note that the sign of the parameter "s" determines whether the expression is for a weak acid or base. Also, each base dissociation constant  $pK_b$  must be converted to an acid dissociation constant  $pK_a$  via Equation 2-3p to use the expressions for bases. If the pH is two units or more larger than the  $pK_a$  for acids or two or more units less than the  $pK_a$  for bases, Equations 2-4d through 2-4f contributes less than 0.01 when summed with 1 in Equations 2-4a through 2-4c. The numerators and denominators are then approximately equal to 1 and Equations 2-4a through 2-4c reduces to



simply  $s \cdot N$ . Thus, the weak acids can be considered completely ionized for a pH greater than the  $pK_a$  by 2 and weak bases can be considered completely ionized for a pH less than the  $pK_a$  by 2. Weak acids behave like strong acids at a high pH and weak bases behave like strong bases at a low pH. The contribution of each weak acid or weak base to the charge balance equation is represented by Equations 2-4a through 2-4c. Equation 2-4g shows the charge balance equation for strong acids and bases and Equation 2-4h shows the charge balance equation for weak acids and bases. The last two terms in both equations are for the hydrogen and hydroxyl ion concentrations.

$$N_1 = \frac{1}{1 + P_1} \cdot s \cdot N \quad (2-4a)$$

$$N_2 = \frac{(1 + 0.5 + P_2)}{(1 + P_2 \cdot (1 + P_1))} \cdot s \cdot N \quad (2-4b)$$

$$N_3 = \frac{(1 + 0.33 \cdot P_3 \cdot (2 + P_2))}{(1 + P_3 \cdot (1 + P_2 \cdot (1 + P_1)))} \cdot s \cdot N \quad (2-4c)$$

$$P_1 = 10^{(s \cdot (pH - pK_1))} \quad (2-4d)$$

$$P_2 = 10^{(s \cdot (pH - pK_2))} \quad (2-4e)$$

$$P_3 = 10^{(s \cdot (pH - pK_3))} \quad (2-4f)$$

For strong acids and bases, the acids and bases are completely dissociated everywhere on the pH scale, which gives the following charge balance:

$$\sum_i N_{bi} - \sum_i N_{ai} + 10^{-pH} - 10^{(pH - pK_w)} = 0 \quad (2-4g)$$

For weak acids and bases with a single dissociation, the concentration of ions depend on pH and are computed via Equation 2-4a, which gives the following charge balance:

$$\sum_i \left[ \frac{1}{(1 + P_{bi})} \cdot N_{bi} \right] - \sum_i \left[ \frac{1}{(1 + P_{ai})} \cdot N_{ai} \right] + 10^{-pH} - 10^{(pH - pK_w)} = 0 \quad (2-4h)$$

where:

- $N$  = concentration of an acid or base (normality)
- $N_1$  = concentration of ions from a single dissociation (normality)
- $N_2$  = concentration of ions from a double dissociation (normality)
- $N_3$  = concentration of ions from a triple dissociation (normality)

$N_{ai}$	=	concentration of an acid $i$ (normality)
$N_{bi}$	=	concentration of a base $i$ (normality)
$pK_1$	=	negative base 10 logarithmic first acid dissociation constant
$pK_2$	=	negative base 10 logarithmic second acid dissociation constant
$pK_3$	=	negative base 10 logarithmic third acid dissociation constant
$pK_w$	=	negative base 10 logarithmic water dissociation constant
$P_1$	=	parameter for an acid or base with one dissociation
$P_2$	=	parameter for an acid or base with two dissociations
$P_3$	=	parameter for an acid or base with three dissociations
$P_{ai}$	=	parameter for dissociation of an acid $i$ with a single dissociation
$P_{bi}$	=	parameter for dissociation of a base $i$ with a single dissociation
$s$	=	ion sign ( $s = -1$ for acids and $s = +1$ for bases)

The titration curves in plants tend to be more buffered than the curves generated by these equations because of the presence of carbonates in plant water. It is suggested that carbon dioxide be added as one of the components in the streams and its concentration adjusted based on the solubility of carbon dioxide at process conditions and titration curves for process samples at normal operating conditions.



*Add carbon dioxide as a stream component and adjust the concentration to provide the buffering effect normally found in plant water.*

For weak acids and bases with double and triple dissociations, Equations 2-4b and 2-4c are used, respectively, in place of Equation 2-4a in Equation 2-4h. Appendix F has a FORTRAN subroutine listing that finds the pH that satisfies the charge balance for  $i$  acids and bases with single, double, or triple dissociations by interval halving. The  $pK_a$  and  $pK_w$  coefficients and the solution density should be corrected for process temperature and composition. The effect of changes in the activity coefficients with ionic strength should also be factored in [Ref. 2.6]. The reader is directed to References 2.4 and 2.8 for a more detailed discussion on the effect of ion concentrations on activity coefficients. The polynomial equation for acid and sodium ion error at the end of the subroutine should be replaced with one that fits the data from the glass manufacturer.



*Adjust the  $pK_a$  and  $pK_w$  in a charge balance model to include the effects of process temperature and ionic strength.*

These equations are of increasing interest to the process control engineer because online charge balance models combined with Coriolis mass flow measurements of influent and reagent flows can provide online fast and reliable pH estimators per Chapter 8. The  $pK_a$  in these models closest to



the pH operating point can be manipulated online by a model predictive controller to match plant data.



An online charge balance model with its  $pK_a$  adapted by model predictive control to match plant data can provide a fast and reliable pH estimator.

## References

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# **Chapter 3: Titration Curves**



## Chapter 3

### Titration Curves

#### 3-1. Slippery Slopes

The task of a conventional control system to maintain a pH set point on the steep slope of a titration curve despite upsets is similar to a novice skier trying to stop on an icy expert slope while being buffeted by high winds.



**Going from a knee to the steep portion of a titration curve can be like falling off a cliff with nothing to break the fall except a knee.**

Unfortunately, most set points are near the neutral or equivalence points on the titration curve, which coincide with location of the maximum slope. After an upset or start-up, the pH accelerates as the operating point approaches the steepest point on the curve. To the pH controller that knows only what it sees, it appears to be a fast runaway or positive feedback response. Most of the beneficial value of the investment in a well mixed vessel in terms of slowing down a disturbance has been lost. The decrease in the effective process time constant seen by the pH controller will be quantified in Chapter 10 on pH control system selection. Operators will ask whether you can do anything to slow down the response because it tends to zip right past the desired set point. In Chapter 8 on pH control systems, we will see how signal characterization can slow down the response by the translation of the controlled variable from pH to percent reagent demand (X axis of the titration curve) to soothe the operator's nerves and restore the process time constant.



**The pH will zoom right past a set point on the vertical portion of the titration curve and most of the beneficial value of the investment in a well mixed vessel in terms of slowing down the nonlinear pH response appears to be lost.**

The pH control system sensitivity and process gain increase as the slope of the titration curve increases. While the details on assessing the exact implications of this statement are covered in subsequent chapters, it is now appropriate to discuss how the slope changes value and location as a



function of stream composition. Figures 3-1a through 3-1d show the changes in the titration curve for four possible combinations of strong and weak acids and bases. In these curves, the strong acid  $pK_a$  and the strong base  $pK_b$  are both 0 and the weak acid  $pK_a$  and the weak base  $pK_b$  are both 4. In every case, the sample is a strong or weak acid titrated with a strong or weak base.

The strong acid and strong base curve shown in Figure 3-1a is distinguished by its vertical slope throughout most of the pH scale range. Figures 1-1b and 1-1c in Chapter 1 showed that this slope is not vertical but changes by a factor of 10 for each pH unit deviation from 7 pH for a solution temperature of 25°C. True titration curves have no straight lines; the blowup of a straight line will reveal another curve if there are enough data points. A titration curve without a clearly defined abscissa is worthless because the shape will change with the abscissa range. Therefore, it is critical to have two titration curves, one that covers the whole operating range and another that details the curvature in the control region.



The shape of a titration curve will drastically change with range of the abscissa and the resolution of the data points in the knees and steeper regions.



*It is critical to have two titration curves, one that covers the whole operating range and another that details the curvature in the control region.*

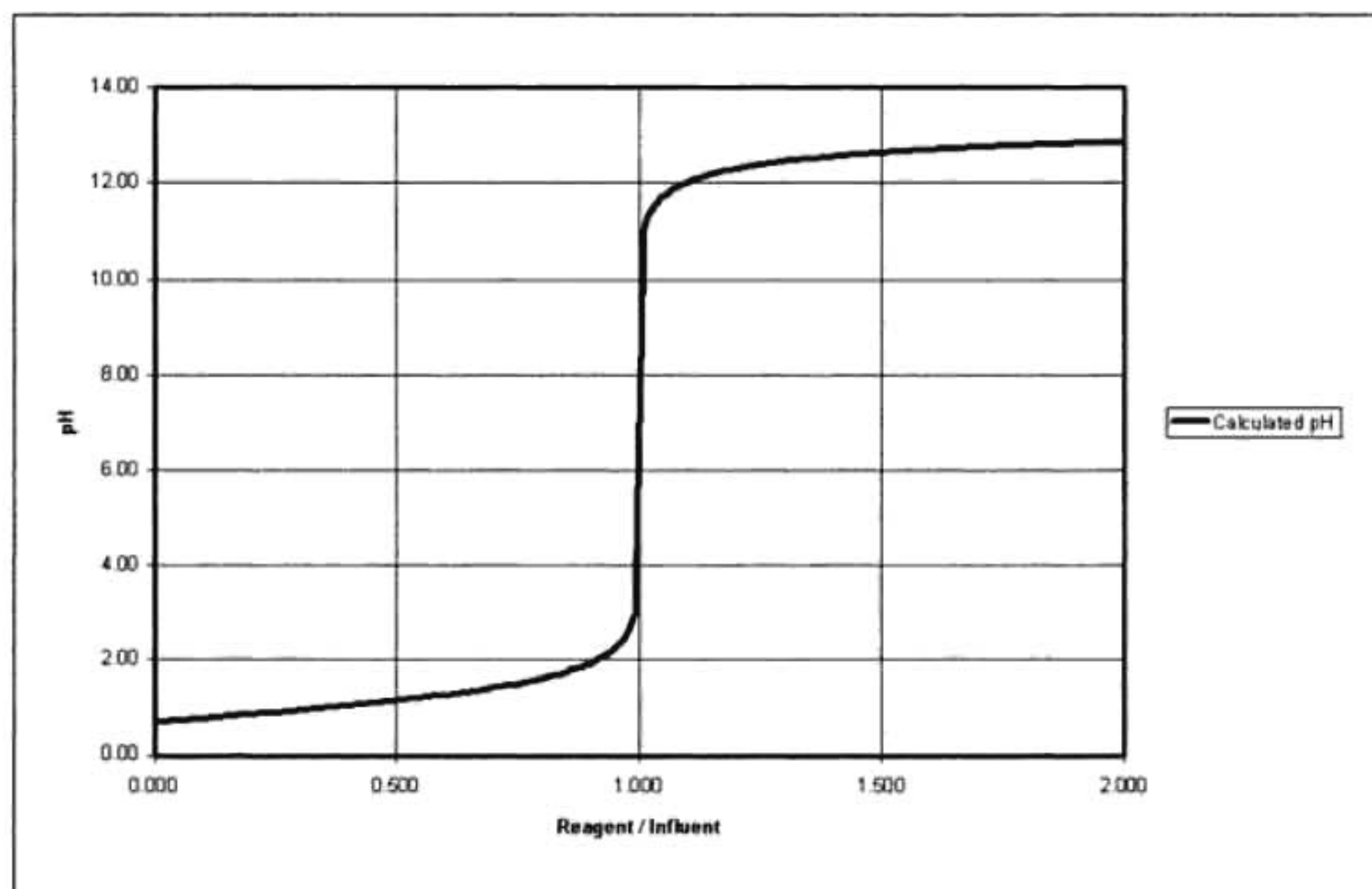
The slope is steepest at the equivalence point. The equivalence point coincides with the neutral point for a strong acid and strong base system. The neutral point occurs at a pH equal to one half of the  $pK_w$  so that its location depends on solution temperature. For example, if the  $pK_w$  decreases from 14.0 to 13.54 because the solution temperature increases from 25°C to 40°C, the neutral point would decrease from 7.0 to 6.77 pH. The definitions of the neutral and equivalence points are as follows:

- The *neutral* point on the titration curve is where the hydrogen ion concentration equals the hydroxyl ion concentration.
- The *equivalence* point on the titration curve is where the acid ion concentration equals the base ion concentration.

While the strong acid and strong base curve in this case and in most textbooks appears to be symmetrical about the equivalence point, the curve is only truly symmetrical if the strong acid  $pK_a$  and the strong base



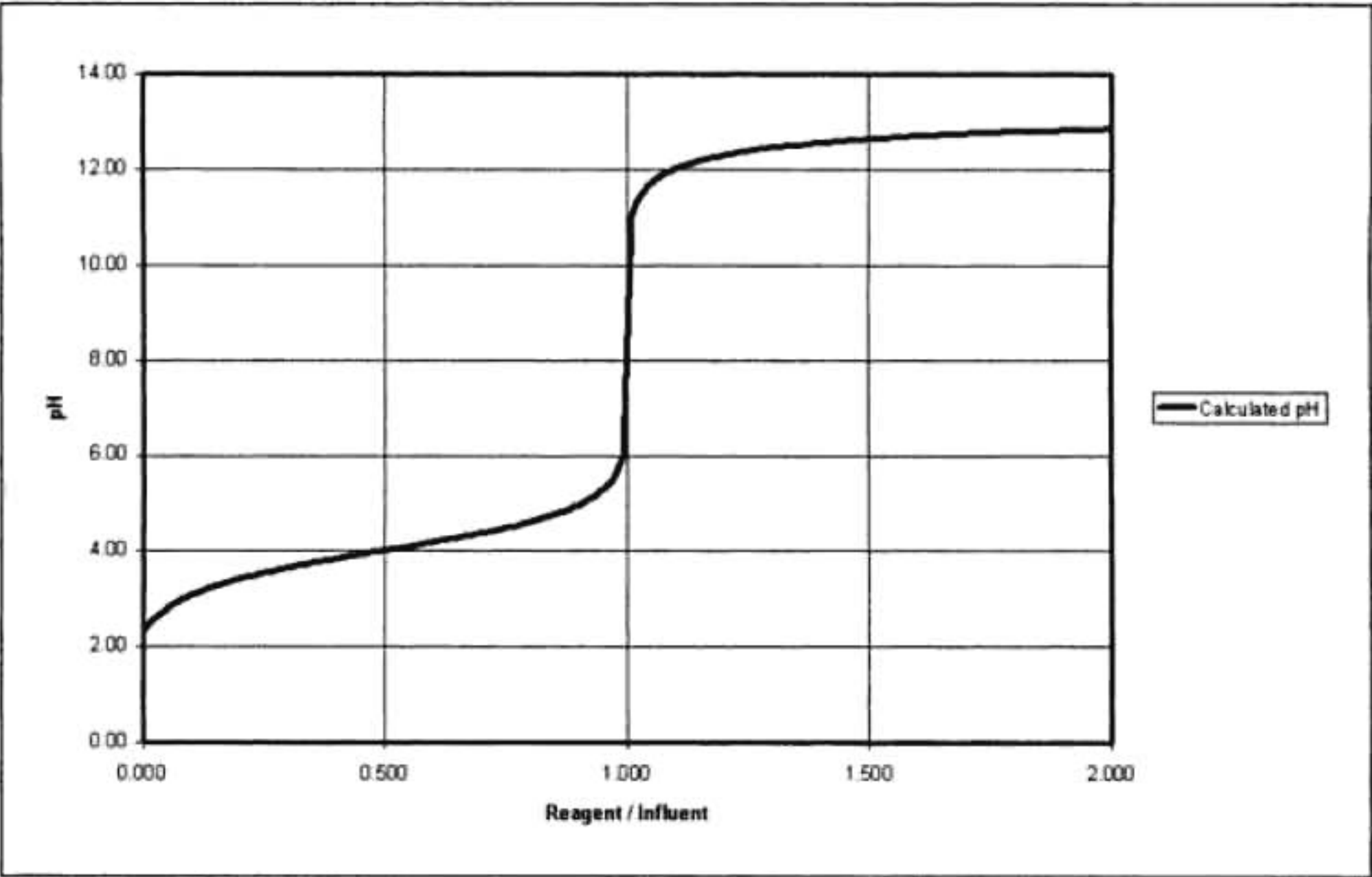
$pK_b$  are equal. The midpoint of the lower flat portion of the titration curve occurs at the pH equal to the  $pK_a$  for the strong acid. The midpoints of the upper flat portions occur at a pH equal to the  $pK_w$  for water and the  $pK_a$  (not the  $pK_b$ ) for the strong base. Two distinct upper flat portions occur if the  $pK_w$  and  $pK_a$  are sufficiently separated. However, the exact shape is difficult to obtain due to the large electrode error and activity coefficient error at these extremes in concentration and is unimportant since it lies outside the practical pH measurement and set point range.



**Figure 3-1a. For a Strong Acid and Strong Base, the Control System Sensitivity and pH Process Gain is a Concern for Almost All pH Set Points**

The strong acid and strong base system has a maximum slope and range of steep slopes greater than any other pH system. The control system sensitivity and the pH process gain is a concern for any pH set point other than at the extremes of the pH scale range.

The weak acid and strong base system in Figure 3-1b is distinguished by its steep slope in the upper pH scale range. The center of this steep slope is the equivalence point location dependent on the dissociation constant of the weak acid. The control system sensitivity and pH process gain is a concern for pH set points greater than 2 pH units above the weak  $pK_a$  and 2 pH units below the strong base  $pK_a$  or the water  $pK_w$ . Thus, for the  $pK_a$  used in this case, the slope is steep between 6 and 12 pH. The sensitivity and gain is least for a pH set point equal to the weak acid  $pK_a$  (4 pH), which is at the midpoint of the lower flat portion. The flat upper and lower ends of the curve are outside the operating pH range.

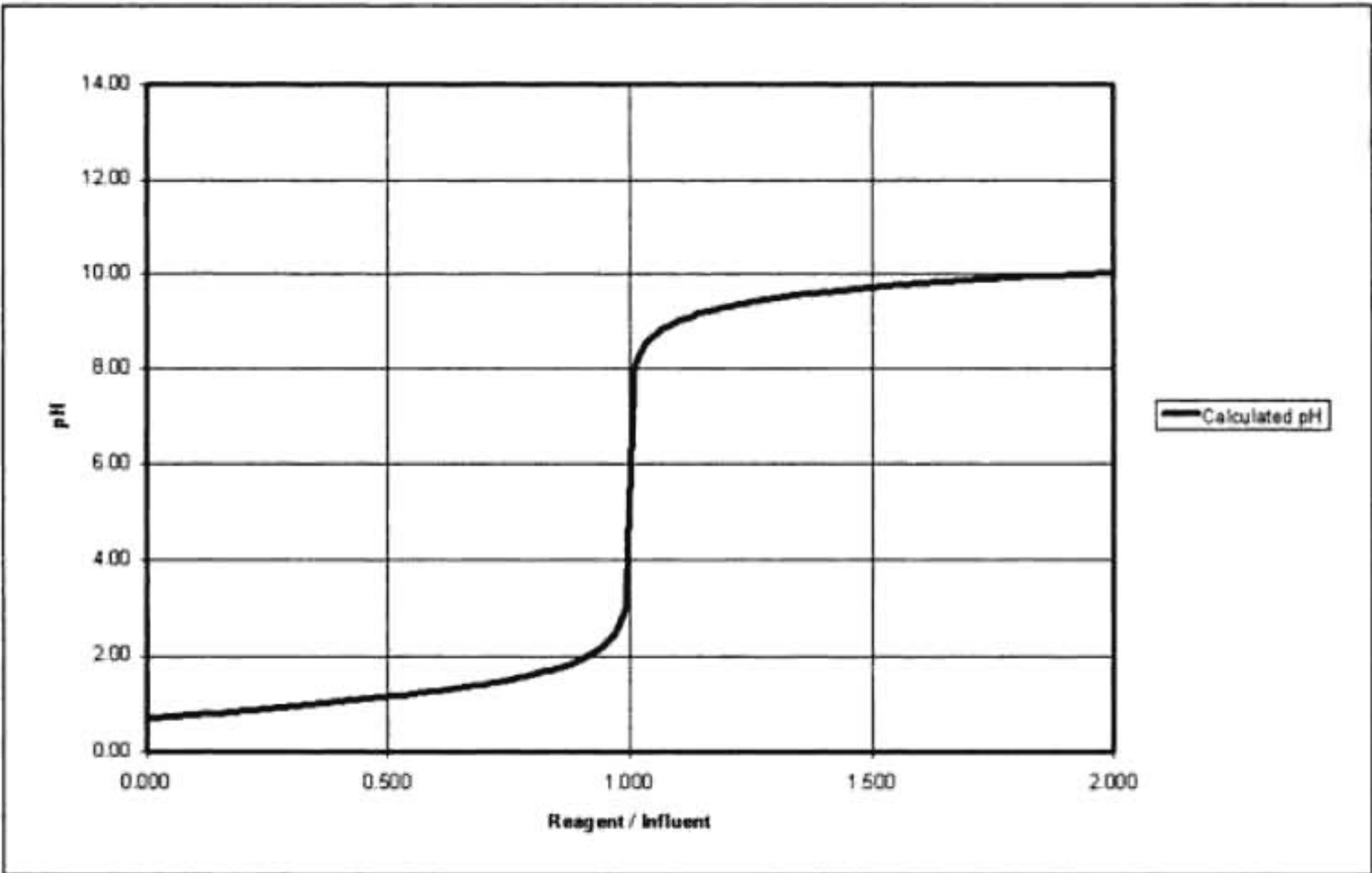


**Figure 3-1b. For a Weak Acid and Strong Base, the Control System Sensitivity and pH Process Gain is a Concern for 6 to 12 pH Set Points**

The strong acid and weak base system shown in Figure 3-1c is distinguished by its steep slope in the lower pH scale range. The center of this steep slope is the equivalence point location dependent on the dissociation constant of the weak base. The control system sensitivity and pH process gain is a concern for pH set points more than 2 pH units below the weak base  $pK_a$  and 2 pH units above the strong acid  $pK_a$ . The sensitivity and gain is least for a pH set point equal to the weak base  $pK_a$  (10 pH), which is at the midpoint of the upper flat portion. Again, the flat upper and lower ends of the curve are not shown since they are outside the operating pH range.

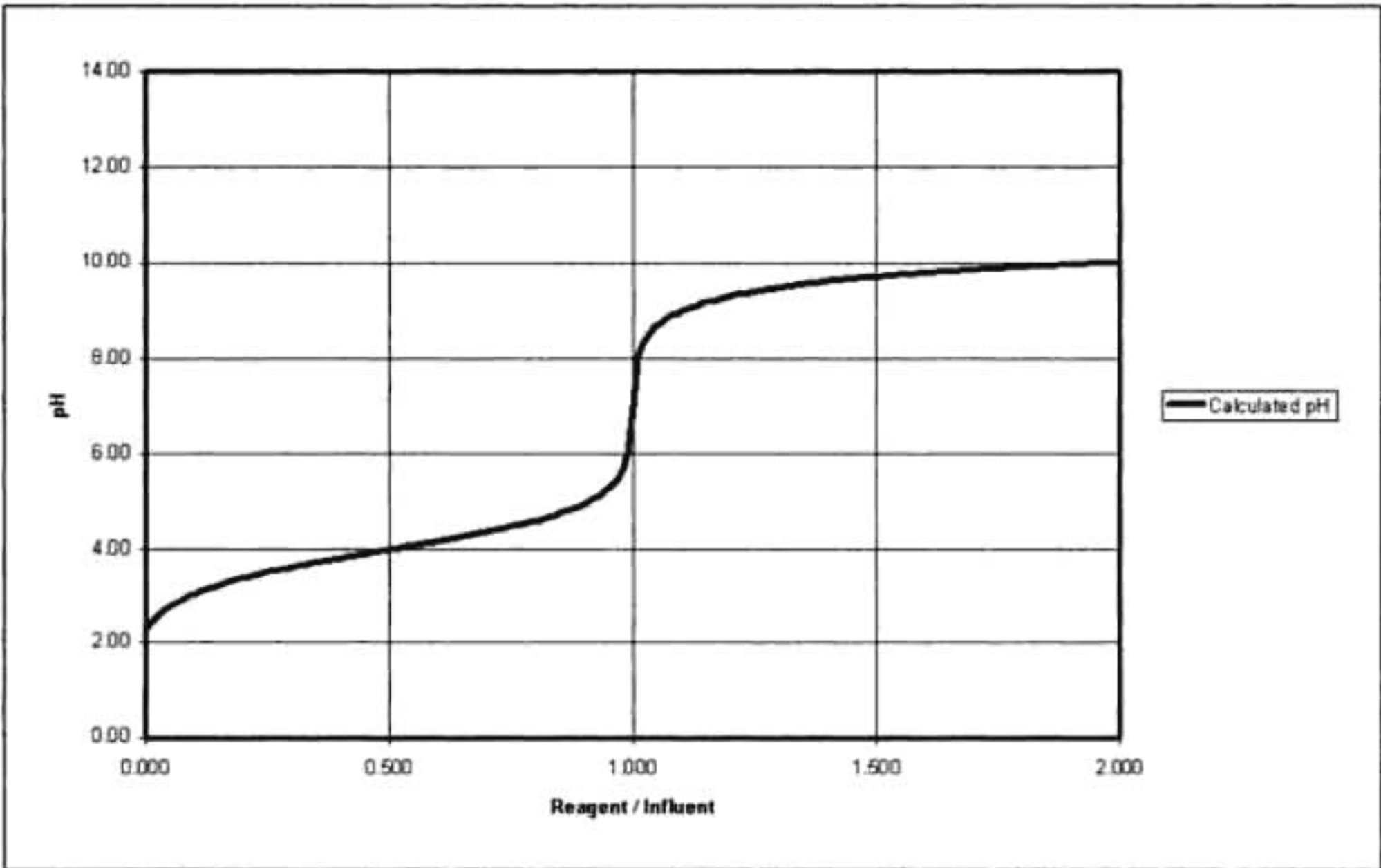
The weak acid and weak base system in Figure 3-1d is distinguished by the lack of a steep slope throughout the range. The titration curve slope is greatest at the equivalence point but is still relatively small compared to the previous systems. The equivalence point ordinate depends on both the acid and base dissociation constants. While the magnitude of the pH process gain is low, the gain is still nonlinear. The system should not be considered easy to control. A common misconception is that a titration curve consists of a single S-shaped curve. In Figure 3-1e, a weak acid with  $pK_a$  dissociation constants at 3 and 5 pH is titrated with a weak base with  $pK_a$  dissociation constants at 9 and 11 pH. Notice that three S-shaped titration curves are formed with an equivalence point at the point of steepest slope for each S. The dissociation constants have to be more than 2 pH units apart to create multiple S-shaped curves. The curves are symmetrical because the concentrations and the distances between the



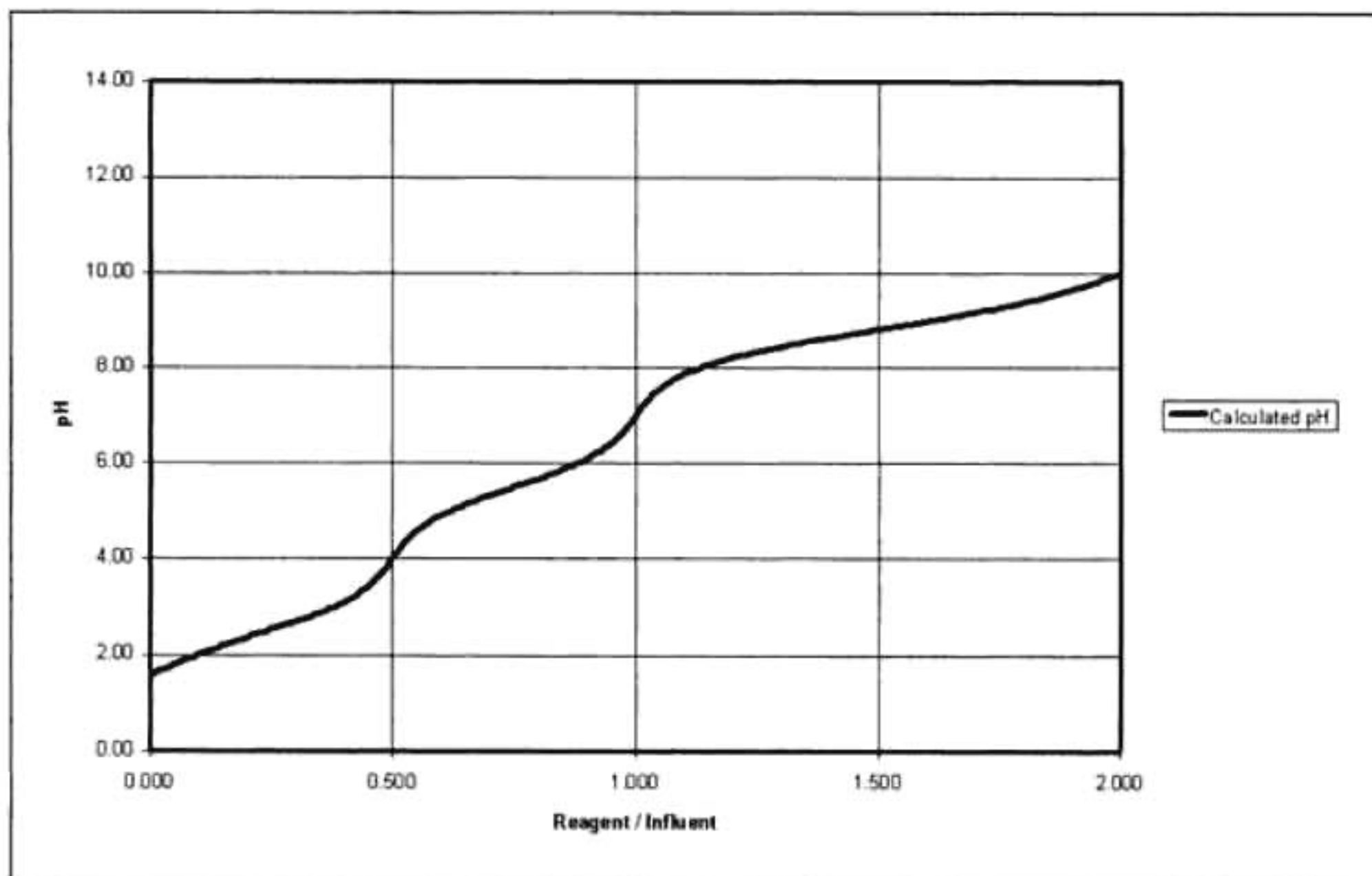


**Figure 3-1c. For a Strong Acid and Weak Base, the Control System Sensitivity and pH Process Gain is a Concern for 2 to 8 pH Set Points**

dissociation constants are equal. Normally pH titration curves are not symmetrical.



**Figure 3-1d. For a Weak Acid and Weak Base, the Control System Sensitivity and pH Process Gain is Moderated Even for Set Points Near the Equivalence Point**



**Figure 3-1e. Multiple S-shaped Curves are Formed from Multiple Weak Acid and Base Dissociation Constants if They Are Spread Apart by More Than Two pH Units**

### 3-2. Laboratory Generation

Laboratory titration curves are typically done by placing a known volume of the process sample in a beaker and logging the pH indication for each incremental volume of reagent added via a burette. The data points are recorded and a smooth curve is plotted between the points. The volume of reagent added between the data points must be reduced drastically near the equivalence point. If the sample or reagent contains a strong acid or base, it is difficult to generate data points near the equivalence point. Most titrators are now automatic with interfaces to plant data historians.

If the titration curve has a long, flat tail, relatively few data points are needed until the first bend. However, in order to estimate the valve rangeability and stick-slip and the mixing equipment size and agitation requirements, the starting point, which represents the influent pH, for various operating conditions must be accurately plotted.

If the sample or the reagent contains solids, the time required for the solids to dissolve and the ions to get into solution to establish the solution ion balance can take from several seconds to several minutes. If the pH has not reached its final value before the reagent volume is incremented, the titration curve becomes distorted. If a gaseous reagent such as ammonia is bubbled into the sample, the wait time between drops must be longer than the dissolution time. Bubbles may rise to the surface and escape from the



solution before dissolving so that the amount of reagent added is not equal to the amount in the solution.

If the volume of the sample is given and the concentration of the reagent used in the laboratory and the control system are equal, the reagent volumetric flow can be calculated for a given influent flow and pH set point per Equation 2-1j. If the concentrations are not equal, then Equation 2-1k is applicable. It is important that the concentration of the laboratory and field reagents be verified before a titration curve is used for system design.

The laboratory temperature during titration is rarely equal to the ambient temperature or process temperature. The sample pH will change with temperature since the dissociation constants and water ionic product change with temperature. This is a change in actual solution pH and is not to be confused with the change in millivolts generated by the glass electrode per the Nernst Equation in Chapter 4. Conventional temperature compensators use a temperature sensor embedded inside the electrode to correct for the Nernst effect.

The sample temperature should be maintained equal to the process temperature at the electrodes by heating or cooling the sample. For greatest accuracy, a separate temperature sensor should be installed at the electrodes and the process temperature made available to the laboratory. If the electrodes are in a recirculation line that is well insulated with no heating or cooling, the vessel temperature can be used. If the process temperature at the electrodes changes by more than a few degrees, multiple samples should be titrated at different temperatures to determine the change in actual solution pH with temperature near the pH set point so that a correction factor can be automatically applied to the field pH measurement based on the deviation from a reference temperature, such as the set point. Most smart field pH transmitters have solution temperature compensation that is a user configurable polynomial to match test results of the change in actual pH with temperature generated in a laboratory. Laboratory pH meters have the conventional electrode temperature compensation that corrects for the Nernst effect but tend not to have solution pH compensation to date. Consequently, if the temperature of the sample cannot be maintained by heating or cooling at the process temperature, a temperature correction must be applied manually or by a special computer program.



**The laboratory pH meters may not have the automatic solution pH temperature compensation configured into the smart field pH transmitter.**



Every sample must be time stamped with the exact time that the sample was taken. Some operators may write the time that they mark the sample or round off or guess at the time. Some operators log the time of the laboratory result. The only way that a laboratory pH measurement result can be correlated with the actual process pH and temperature recorded in the data historian, is to have the sample correctly time stamped.



*The sample and the curve should be marked with the exact time the sample was taken and the process temperature at the electrode.*



*The laboratory meter and the field transmitter must use the same algorithm for solution temperature compensation.*

Samples should be kept in Pyrex glass or polyethylene plastic bottles. Soft glass bottles should not be used because the glass solubility is great enough to raise the pH due to the absorption of alkali ions by the sample. Cork stoppers should not be used because the corks are highly acidic. Samples exposed to the air can absorb enough carbon dioxide to lower the pH. This is a particular problem for nearly pure water and caustic samples. The pH of absolutely pure water at 25°C can change from a pH of 7 to a pH of 5.7 by exposure to air. The slope of caustic solutions will decrease in the region of 6 to 7 pH from the moderating effect of carbonates due to the absorption of carbon dioxide from the air. This moderating effect of carbonates helps to regulate the pH of many aquatic streams and reduces the difficulty of waste and raw water pH control. References 3.1 and 3.2 have information on the effect of carbon dioxide on the pH of samples.



*Samples should be kept in closed Pyrex glass bottles to reduce the change in composition of the sample from evaporation and absorption.*

The errors at the high and low ends of the pH scale depend on the type of pH electrode, process chemicals, and the time and temperature exposure. Acidic solutions below 2 pH can dehydrate the glass electrode. Hydrofluoric acid solutions below 4 pH and caustic solutions above 10 pH can chemically attack the glass. Both chemical attack and dehydration are greatly accelerated by temperature. In general, a higher electrical resistance of the glass translates to a greater chemical resistance. Also, there are glasses specifically designed for low and for high pH operation. High concentrations of relatively small alkali ions such as sodium ions can also penetrate the glass and suppress the pH reading, although this alkalinity error is less of a problem for newer glass designs. The type of glass needs to be chosen to minimize the effect of the largest error.



High ionic strength streams can also cause a slow drift in liquid junction potential of the reference electrode. For certain types of electrodes and process conditions, it can take hours for the reference electrode to reach an equilibrium state. In cases of contamination of the internals of the reference, the drift does not stop but continues. The best method of reducing junction potential errors and contamination is a flowing junction reference, but the flow rate of electrolyte must be small enough not to contaminate the sample.

Since the immersion time of laboratory electrodes is much shorter than the exposure time of field electrodes, most of the effect of the process on the glass and reference electrodes does not take place to the same degree in the laboratory as in the field. In fact, this is the key to how to deal with really nasty streams. Chapter 4 will discuss using automated injection assemblies to control the time of exposure of field electrodes to the process.



**The short immersion time of laboratory electrodes reduces the errors from the chemical attack and dehydration of the glass of the measurement electrode and the drift of the liquid junction potential of the reference electrode.**



***The laboratory and field measurement electrodes should use the same type of glass selected to minimize the effects of process conditions.***

If the titration curve changes with time, separate samples should be gathered over a representative period and individually titrated. The samples should not be combined for titration. The pH controller sees individual titration curves, not a composite. This and the other common problems that reduce the utility of laboratory titration curves are listed in Table 3-2a.

The development of titration curves for split ranged pH control systems should take into account the sequence of reagent addition, the degree of back mixing, and effect of overshoot and oscillation at the point of transition between split-ranged valves. Of course, if the split ranging consists of a small and large valve on the same reagent, there is just one reagent required in the titration and these special considerations are not applicable.

In an inline control system such as a static mixer, there is no back mixing so the history of reagent addition can be ignored in the generation of the titration curve. If there is a simple split range between an acid and a base

**Table 3-2a. Common Problems with Laboratory Titration Curves**

1. An insufficient number of data points were generated near the equivalence point.
2. The starting pH (influent pH) data points were not plotted for all operating conditions.
3. The curve doesn't cover the whole operating range including control system overshoot.
4. No separate curve zoom-in to show the curvature in the control region.
5. There is no separate curve for each different split-ranged reagent.
6. The effect of the sequence of the different split-ranged reagents was not analyzed.
7. The effect of back mixing of different split-ranged reagents was not considered.
8. The effect of overshoot and oscillation at the split-ranged point was not included.
9. The sample or reagent solids dissolution time effect on the abscissa was omitted.
10. The gaseous reagent dissolution time and escape effect on the abscissa was omitted.
11. The sample volume was not specified.
12. The sample time was not specified.
13. The reagent concentration was not specified.
14. The sample temperature during titration was different than the process temperature.
15. The influent sample was contaminated by absorption of carbon dioxide from the air.
16. The influent sample was contaminated by absorption of ions from the glass beaker.
17. The influent sample composition was altered by evaporation, reaction, or dissolution.
18. The laboratory and field measurement electrodes had different types of glass.
19. A composite sample instead of individual samples was titrated.
20. The laboratory and field reagents used different compounds.



reagent because the influent can come in acidic or basic, then a titration curve can be generated based on titrating an acid reagent into a basic influent and a base reagent into an acidic influent.

If a well-mixed vessel is used, there is by design back mixing, which means the sample can be a mixture of influent, effluent, and reagents. The ratio of reagent to influent is still based on the incoming stream before reagent addition, so the same curves described for the inline mixer are still needed. However, additional curves should be generated in the control region that includes the addition of one reagent to overshoot the set point to the allowable control error, which is the limit of the control region, and the titration of the other reagent to bring the pH back to the set point.

If there are different types of basic or acid reagents, such as might occur because of the preferential use of a lower cost or waste stream as a reagent, then there should be a separate titration curve for each reagent that takes into account the sequence regardless of the degree of back mixing. A curve should be generated with the influent sample titrated with the first reagent in the split range sequence. Additional curves should be generated by the titration of the second reagent into a sample with the first reagent added according to the minimum and the maximum ratio achievable based on maximum reagent valve capacity and the minimum and maximum influent flow and pH. If there is back mixing, then again overshoot from one reagent and back titration of the other reagent in the control region should also be explored. Needless to say, these scenarios are hardly ever properly addressed or even realized and the chances of getting it right are slim to none unless there is detailed analysis of what the control system can see in terms of a variety of mixtures of influent and reagents.



To create samples with the proper influent and reagent mixtures from split ranged reagents requires understanding the sequence of the split ranged operation and whether back mixing creates a history of reagent addition.



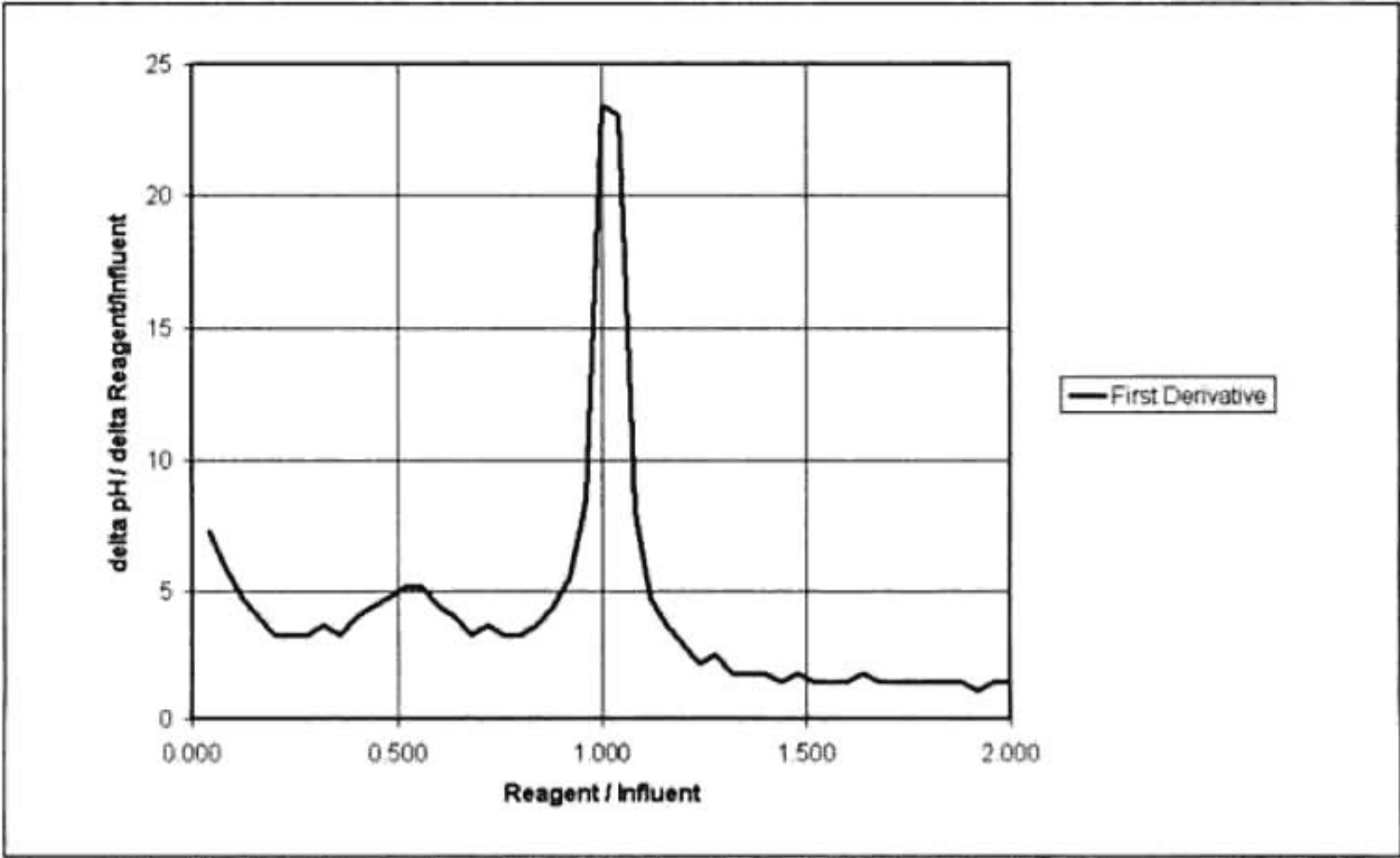
*The preferential use of a low-cost reagent requires curves be generated for the titration of the low-cost reagent into an influent sample and the titration of the high-cost reagent into a mixture of the influent and low-cost reagent.*



*If there is back mixing, then additional curves should be generated in the control region for a mixture of the influent and the overshoot of one reagent and the titration of the other reagent to return the pH to the set point.*



Automatic titrators that are electronically equipped to compute the first and second derivative of pH with respect to time, and hence reagent flow, can automatically locate the equivalence point. The first derivative, which is the slope of the titration curve, reaches a maximum at the equivalence points. The second derivative changes sign at the equivalence points. A plot of first derivative helps in the control system design because it is indicative of the pH process sensitivity. Figure 3-2a shows a plot of the first derivatives for the weak acid and weak base titration curve in Figure 3-1e. For more information on automatic titrators, consult Reference 3.3.



**Figure 3-2a. The First Derivative of the Titration Curve is Indicative of the Process Sensitivity, Which Reaches a Maximum at the Equivalence Points**

### 3-3. Computer Generation

The FORTRAN subroutine in Appendix F solves the charge balance equation described in Chapter 2 and computes the pH and ion concentrations for any number of acids and bases each with up to three dissociation constants. It does not have activity coefficients. It is designed to be called from another program that provides the proper input data. If the types and quantities of acids and bases are not known, or the effect of the activity coefficients is important, an optimization program can be used to adjust the input data such as acid or base weight fraction or dissociation constant to minimize the error between it and a laboratory or more accurate computer-generated titration curve. The main advantage of the subroutine in Appendix F is its relative computational simplicity, which allows it to be used in dynamic simulation programs without lengthy run



times. The interval-halving search method is simple and efficient. While the Fibonacci method has proven to be successful, many other search methods develop instabilities due to the large concentration range covered for pH calculations. For more information on the problems with iterative search techniques for pH, the reader is directed to Reference 3.4.



*An interval halving search to find the pH that satisfies the charge balance is the most efficient method to compute pH for a complex mixture.*

Dynamic simulation programs must have double precision instead of single precision arithmetic to show pH control of a strong acid and strong base; otherwise, round-off error in the concentration calculation can cause an error of about one pH unit near the equivalence point. The weight fractions for inline systems are based simply on the ratios of component mass flows to total flow, but in vessels the net component mass flows in and out of the volume are integrated to accumulate each component's mass. Variable step integration methods develop problems due to noise from interval halving and the high sensitivity of the pH process. Fixed-step integration methods provide accuracies well within the limits of pH measurement and control in the field. Figure 3-3a shows the programming blocks and inputs needed for dynamic simulation of a pH vessel.



*Double precision math is needed to compute pH for a strong acid or base system.*



*Fixed step integration techniques should be used for dynamic simulation of strong acid or bases.*

If a more accurate computer-generated titration curve is needed, the Equilibrium Composition of Electrolyte Solutions (ECES) program from OLI Systems, Inc. can be used for steady-state modeling of aqueous electrolyte systems. The program first generates a set of algebraic equations describing the equilibrium conditions from the user-defined chemistry and physical properties. The program then solves the equations simultaneously for the unknown values based on a set of known values supplied by the user. The program may develop convergence problems for particularly difficult systems. While the program has a library of physical properties, such as activity coefficients, the user frequently has to find or estimate input data for the program. For more information on the capabilities of the ECES program, the reader is directed to Reference 3.5.

The effect of solution ionic strength on the acid dissociation constants can be estimated for relatively dilute solutions by the use of Equation 2-3q and

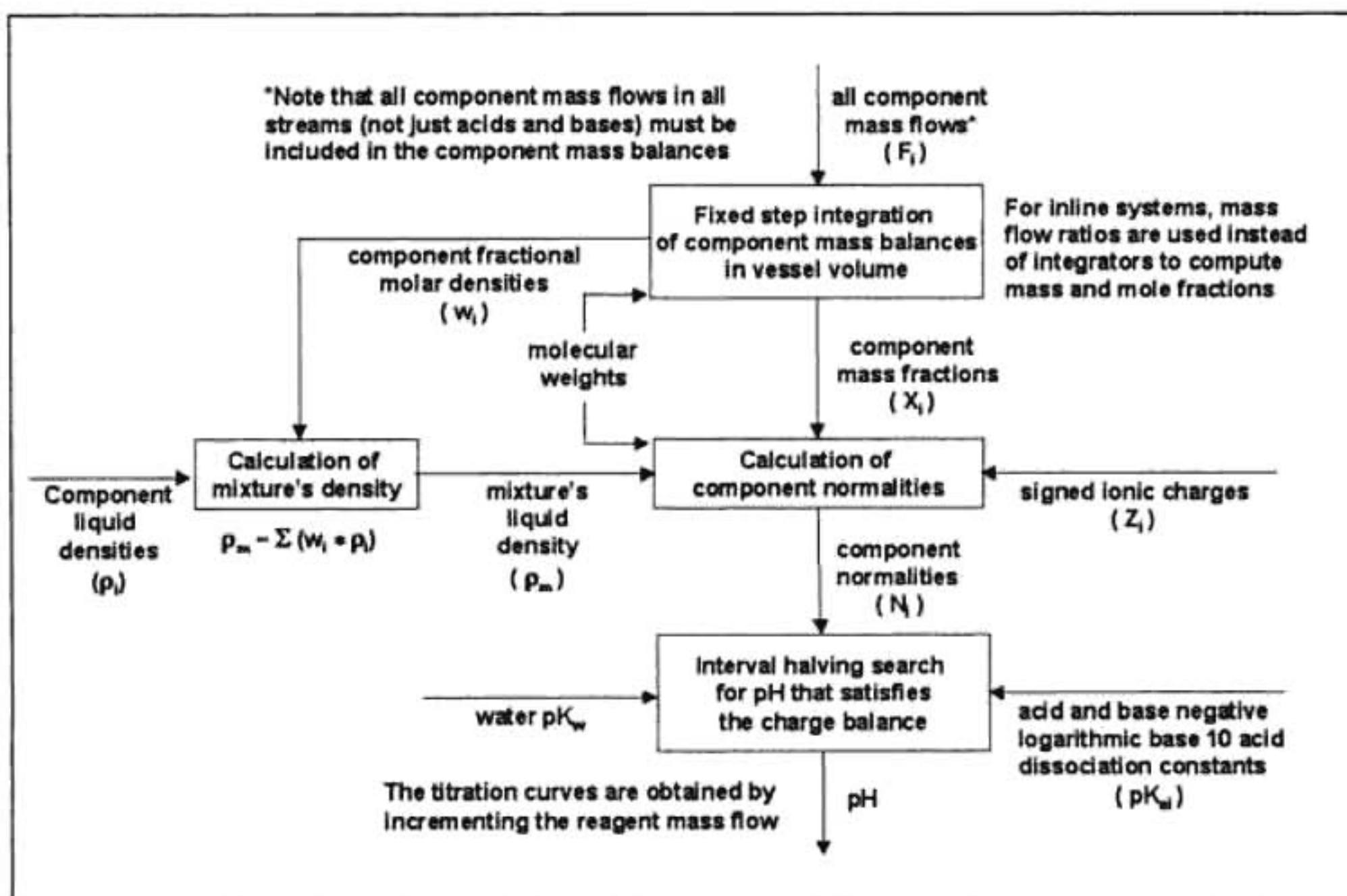


Figure 3-3a. Dynamic Simulation of a pH Vessel Requires the Integration of All Component Mass Balances and an Interval Halving Search for a Charge Balance

Reference 3.6. The  $pK_a$  dissociation constant and the A parameter are functions of the process temperature.

### 3-4. Field Generation

The titration curve can be field generated by measuring and keeping the influent flow constant, slowly ramping the reagent flow to an inline mixer, and using a data historian to plot the pH measurement versus a delayed ratio of reagent to influent flow. The delay time applied to the ratio should be equal to the sum of the electrode lag time and the process time delay, which is the reagent transportation delay from the reagent valve to the pH electrode. The filter time applied to the ratio should be equal to the filter time used on the pH signal. The curve should have the proper shape if the pH is sufficiently filtered, the data historian compression and highway exception reporting settings are small and fast enough, and the reagent ramp time is slower than ratio delay time and the flow controller's integral time, which in turn should be slower than the stroking time of the reagent control valve. If the ramp time is 1 minute or larger, the reagent flow controller should be able to keep up with the ramping set point, and the distortion of the pH from the sensor lag time should be minimal. An inline system is preferred, because there is negligible back mixing and consequently doesn't have the distortion that occurs in a well-mixed vessel where there is a prior history of reagent addition and a large



process time constant, which is approximately the vessel residence time. A vessel could be titrated in the fed-batch mode, where the discharge flow is shut off but the feed continues; however, the ramp time must be much slower and the amount of off-spec material created from the test is much larger than it is for an inline mixer. The process delay is now the sum of a reagent transportation delay and vessel turnover time. Conventional dip tube design causes a huge reagent delivery delay. Special methods of reagent injection detailed in Chapter 5 must be employed or else the time shift will make a field titration curve impossible.



*The X axis ratio should be dimensionless and be delayed by a time equal to the sum of the process time delay and electrode lag time for the field generation of titration curves.*

If the influent flow is also shut off to the vessel so that it is in the full batch mode, and its level, weight, or initial charge can be accurately measured, then a technique similar to that used in a laboratory titration can be mimicked in the field. The vessel acts as a huge beaker. The ratio is now the reagent flow divided by the initial vessel contents. Of course, the ratio should be dimensionless, so if the reagent has a mass flowmeter, the initial vessel contents should be expressed as a weight. Load cells or, even better, a mass flow totalizer for the initial charge provides the best accuracy. The tank level should be low to minimize the reagent required and the amount of off-spec material created. To show the shape of the curve for overshoot, the ramp must cause the pH to go beyond the set point.

Inline systems will be shown to have advantages in Chapters 8 through 10 for pH control in terms of the speed of start-up and tuning, and the capital investment. Here we see they also have an advantage for the field generation of titration curves. The upset created from a test to generate the titration curve via an inline system is usually attenuated enough by a downstream volume so that the effluent or product stays within the desired control region. However, if such tests are not allowed, an inline system can still facilitate online identification while the controller is in automatic. Data points are gathered and matched with a delayed ratio of reagent to influent flow. For larger upsets and startup, a significant portion of the titration curve can be updated. For tight control, the region is naturally small but accordingly, a wider view is not as important. The automatic updating of the curve is especially useful for the tuning and signal linearization of waste treatment systems where there is a large variability in the composition of the influent and consequently the shape of the titration curve. Figure 3-4a shows the setup of an inline system for automated field generation of titration curves.



An inline system can facilitate the field generation of a titration curve by preprogrammed tests or by online identification during upsets and startup.

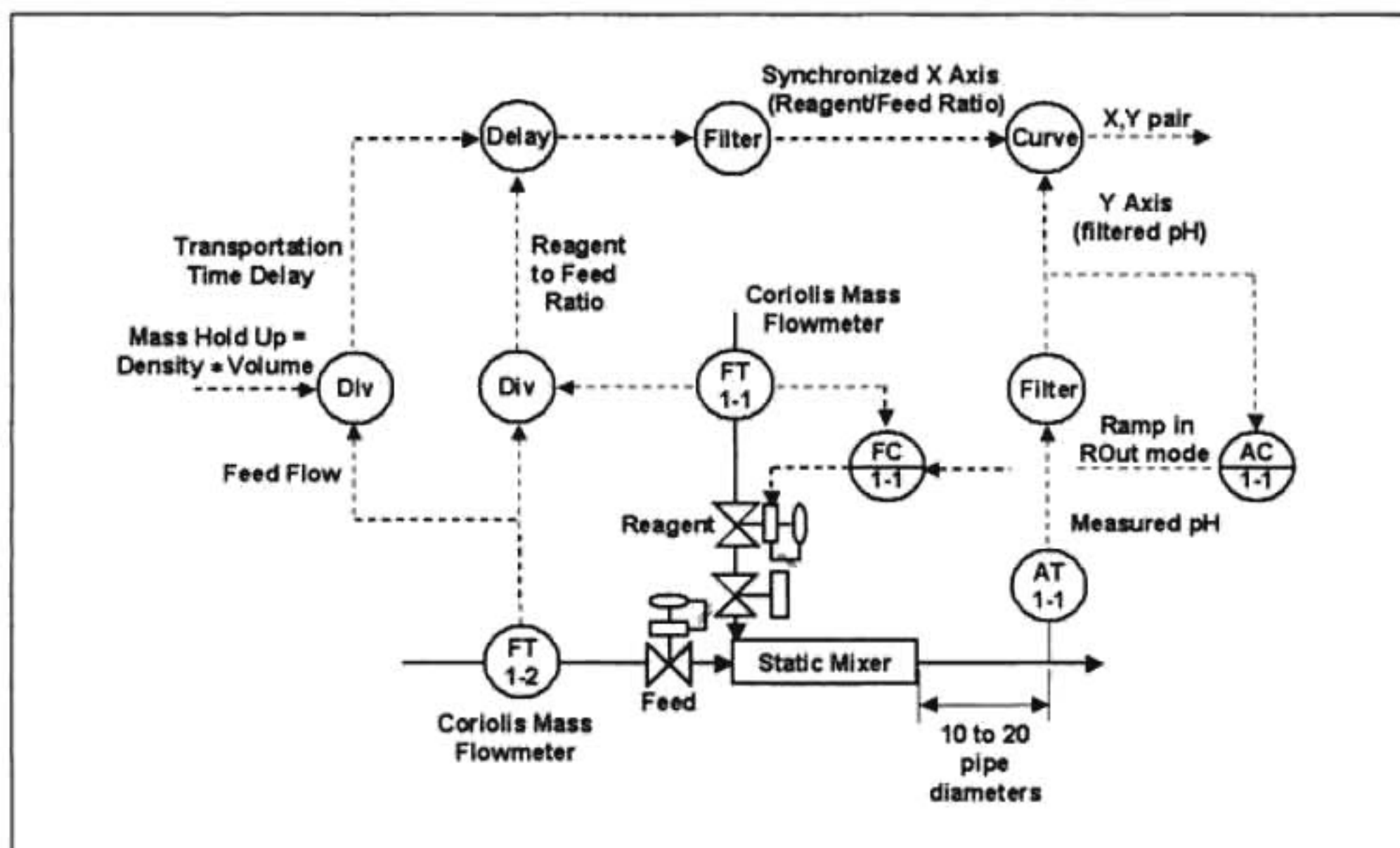


Figure 3-4a. An Inline pH Control System with Its Short Residence Time and Plug Flow Facilitates a Relatively Fast Automated Field Generation of the Titration Curve

### 3-5. Buffering

Some titration curves have a long region of relatively flat slope. The addition of reagent in this portion of the titration curve has little effect on the pH. This flatness of the curve can be due to buffering, which occurs for mixtures of a weak acid or a weak base and its salt. It is also important for keeping solutions used for calibration at a known pH despite contamination from residue on the electrode. Some of the more commonly encountered buffer systems are acetic acid-acetate, carbonic acid-bicarbonates, and citric acid-citrates.

Equations 3-5a through 3-5f shows the source of the buffering effect. Equation 3-5a is the dissociation of an acetic acid-acetate system solved for the hydrogen ion concentration. By taking the negative base 10 logarithm of both sides of this equation as shown in Equation 3-5b, we can convert from  $K_a$  to  $pK_a$  and from  $[H^+]$  to pH to yield Equation 3-5c (a unity activity coefficient is assumed here). In the buffered region, the concentrations of acetate ions  $[Ac^-]$  and the unionized acetic acid  $[HAc]$  are very large with respect to the hydrogen ion  $[H^+]$  concentration. If hydrochloric acid residue from cleaning and rejuvenating the glass



electrode gets into the solution, the large concentration of acetate ions quickly converts the extra hydrogen ions to unionized acetic acid. If the contaminant is a base such as sodium hydroxide, the extra hydroxyl ions neutralize hydrogen ions but these hydrogen ions are quickly replaced by the ionization of acetic acid. The percent change in the unionized acetic acid and acetate ions is small because the magnitude of these concentrations is large. The ratio of acetic acid to acetate concentration is relatively constant so that the hydrogen ion concentration and pH stays the same for a constant temperature and thus constant  $pK_a$ . In buffer solutions, the ratio of the weak acid to its salt or weak base to its salt is nearly unity so that the pH is approximately equal to the  $pK_a$ , which is the point of maximum buffering. Buffer solutions are used for checking the accuracy of pH electrodes because the pH of the test solution remains constant even after moderate contamination. The buffer value is a measure of the ability of the buffer solution to resist pH change and is defined as the gram-moles per liter of a strong acid or base needed to change the pH by one unit.

Solving the dissociation equation for the hydrogen ion concentration, we have:

$$[H^+] = \frac{[HAC]}{[AC^-]} * K_a \quad (3-5a)$$

Taking the negative base 10 logarithm of both sides provides:

$$-\log[H^+] = -\log \frac{[HAC]}{[AC^-]} - \log[K_a] \quad (3-5b)$$

Substituting in the definition of pH and  $pK_a$  and inverting the concentration ratio gives:

$$pH = \log \frac{[AC^-]}{[HAC]} + pK_a \quad (3-5c)$$

For acid buffer solutions this corresponds to:

$$pH = \log \frac{C_{salt}}{C_{acid}} + pK_a \quad (3-5d)$$

For base buffer solutions, it can be shown:

$$pH = \log \frac{C_{base}}{C_{salt}} + pK_w - pK_b \quad (3-5e)$$

A conversion from  $pK_b$  to  $pK_a$  per Equation 2-3l yields:

$$pH = \log \frac{C_{\text{base}}}{C_{\text{salt}}} + pK_a \quad (3-5f)$$

where:

- $Ac^-$  = acetate salt ion concentration (normality)
- $HAc$  = unionized acetic acid concentration (normality)
- $H^+$  = hydrogen ion concentration (normality)
- $K_a$  = acid dissociation constant
- $C_{\text{acid}}$  = molar concentration of the weak acid (gm-moles per liter)
- $C_{\text{base}}$  = molar concentration of the weak base (gm-moles per liter)
- $C_{\text{salt}}$  = molar concentration of the salt ion (gm-mole per liter)
- $pK_a$  = negative base 10 logarithmic acid dissociation constant
- $pK_b$  = negative base 10 logarithmic base dissociation constant
- $pK_w$  = negative base 10 logarithmic water dissociation constant

The above equations show that a solution weak acid or base concentration close to the concentration of its salt will provide a constant pH equal to the  $pK_a$  of the acid or base.

### 3-6. Uses

The titration curve is the single most important piece of information for the design, commissioning, and troubleshooting of pH control systems. The uses listed in Table 3-6a will be discussed in subsequent chapters.

**Table 3-6a. Titration Curves Have Many Important Uses for a Successful Application**

- |    |  |
|----|--|
| 1. | Assessment of application difficulty.                            |
| 2. | Estimation of steady state process gain.                         |
| 3. | Selection of best set point for each stage.                      |
| 4. | Approximation of nonlinearity effect on mixing time constant.    |
| 5. | Inclusion of nonlinearity effect on control loop errors.         |
| 6. | Linearization of controlled variable by signal characterization. |
| 7. | Calculation of continuous pH feedforward signal.                 |
| 8. | Specification of ratio factor for flow feedforward.              |



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# **Chapter 4: Electrodes**



## Chapter 4

### Electrodes

#### 4-1. A Dose of Reality

The incredible sensitivity and rangeability of the pH measurement is based on a series of assumptions, most of which are not sufficiently explained in the literature. Manufacturers have been doing a better job at noting some considerations, especially as they develop new electrode features that can address a particular application problem. In this section, equations are presented that reveal underlying assumptions to help the user cut through the hype. With pH electrodes more than with any other sensor, there is a need to “keep it real.”

The accuracy and speed of response of the pH measurement depends on the condition of a hydrated gel layer on the surface of the glass electrode that is only  $10^{-4}$  mm thick and the condition of a junction of the reference electrode that provides a physical contact between its internal electrolyte and the process solution. The need for the gel layer and the process junction of the reference to be structurally consistent, clean, and free from contamination has profound implications for the proper selection, calibration, and maintenance of pH measurements. The fact that pH sensors perform as well as they do despite exposure to a wide variety of chemicals, temperatures, and pressures is truly remarkable and testimony to the ingenuity of various electrode designs.



The accuracy and speed of response of pH measurements stated in the literature assume the thin gel layer of a glass electrode and the porous process junction of the reference electrode have had no penetration or adhesion of the process (in perfect condition), and the solution is a buffer at room temperature.

The pH measurement and reference electrodes each have an internal galvanic half-cell. The measurement and reference electrode half cells typically both consist of a silver wire with a silver chloride coating at its end immersed in a solution with chloride ions as shown in Figures 1-4a and 1-4c in Chapter 1. The reference electrode fill is usually a concentrated potassium chloride solution for aqueous processes while the measurement electrode fill is usually a chloride buffer with a hydrogen activity equivalent to 7 pH.



The actual sensing of pH is accomplished by having a pH-sensitive glass in contact with the internal fill, a 7 pH buffer, and the external solution. The pH-sensitive glass develops potentials per Equations 4-1a and 4-1d, which are Nernst equations, by the hydrogen ion (proton) exchange between hydronium ions in aqueous solutions and in the hydrated gel layer of the glass. The migration of hydronium ions through the boundary layer that surrounds the surface takes several seconds even under the best of conditions, but once the hydronium ions are in close proximity to the surface, protons jump from the hydronium ions and become associated with water molecules on the surface. There is no migration of hydronium ions intact into the surface but rather a proton transfer that occurs for aqueous and non-aqueous solutions [Ref. 4.1, 4.2, and 4.3]. As protons move into one surface from a greater dissociation of hydrogen ions, they move out of the surface on the other side of the glass. Lithium and sodium ions in the dry interior of the glass provide the electrical continuity between the internal and external hydrated gel layers. Thus, current flow through the glass consists of the conduction of single charged positive ions (cations). The potential developed is proportional to the difference in logarithms of the activity of hydronium ions in solution and in the gel layer on each side of the glass membrane. If the gel layers have an equal number of sites for proton exchange, the constants  $K_{g1}$  and  $K_{g2}$  will be equal and Equations 4-1c and 4-1e can be combined to yield Equation 4-1f. If all the original lithium or sodium ions at these sites in the gel are also replaced by protons, the activities  $a_{g1}$  and  $a_{g2}$  are equal, which yields Equation 4-1g [Ref. 4.3]. By use of the definition of pH, the logarithms of hydrogen activity can be converted to pH, which yields Equation 4-1h, where the difference in potentials is proportional to the difference in pH. Also, since the internal fill has a hydrogen activity that corresponds to 7pH, the potential difference becomes Equation 4-1i, which is the equation that is typically shown in the literature. Examination of this simplified equation for the ideal pH measurement electrode yields the following conclusions:

1. At 25°C, the output decreases from +480 mV at 0 pH to -480 mV at 14 pH.
2. The output is 0 mV at 7 pH.
3. There is no effect of temperature changes on the electrode output at 7 pH.
4. At 25°C, the output changes by 59 mV per pH unit.

The general Nernst Equation:

$$E_1 = E_0 + \frac{R * (T + 273.16)}{F} \quad (4-1a)$$



For the exterior surface of the pH glass electrode:

$$E_1 = K_{g1} + 0.1984 * (T + 273.16) * \log \left[ \frac{a_1}{a_{g1}} \right] \quad (4-1b)$$

$$E_1 = K_{g1} + 0.1984 * (T + 273.16) * [\log(a_1) - \log(a_{g1})] \quad (4-1c)$$

For the interior surface of the pH glass electrode:

$$E_2 = K_{g2} + 0.1984 * (T + 273.16) * \log \left[ \frac{a_2}{a_{g2}} \right] \quad (4-1d)$$

$$E_2 = K_{g2} + 0.1984 * (T + 273.16) * [\log(a_2) - \log(a_{g2})] \quad (4-1e)$$

If  $K_{g1} = K_{g2}$ , then:

$$E_1 - E_2 = 0.1984 * (T + 273.16) * [\log(a_1) - \log(a_{g1}) + \log(a_{g2}) - \log(a_2)] \quad (4-1f)$$

If also  $a_{g1} = a_{g2}$ , then:

$$E_1 - E_2 = 0.1984 * (T + 273.16) * [\log(a_1) - \log(a_2)] \quad (4-1g)$$

Since  $\text{pH}_1 = -\log(a_1)$  for external process and  $\text{pH}_2 = -\log(a_2)$  for internal electrolyte:

$$E_1 - E_2 = 0.1984 * (T + 273.16) * (\text{pH}_2 - \text{pH}_1) \quad (4-1h)$$

Since the internal buffer of the glass electrode is 7 pH:

$$E_1 - E_2 = 0.1984 * (T + 273.16) * (7 - \text{pH}_1) \quad (4-1i)$$

where:

- $a_1$  = activity of hydrogen ions in external process fluid (normality)
- $a_2$  = activity of hydrogen ions in internal fill fluid (normality)
- $a_{g1}$  = activity of hydrogen ions in outer gel surface layer (normality)
- $a_{g2}$  = activity of hydrogen ions in inner gel surface layer (normality)
- $E_1$  = potential developed at external glass surface (millivolts)
- $E_2$  = potential developed at internal glass surface (millivolts)
- $F$  = Faraday Constant (94487 C/ mol, C is an abbreviation for coulomb)
- $K_{g1}$  = constant for potential for outer gel surfaces layer (millivolts)
- $K_{g2}$  = constant for potential for inner gel surfaces layer (millivolts)
- $\text{pH}_1$  = pH of external solution
- $\text{pH}_2$  = pH of internal solution (typically 7 pH)

R = Ideal Gas Constant (8.314 J/ mol\*K)  
T = solution temperature (°C)



The equation for the calibration of the glass electrode assumes the point of zero temperature effect and 0 mV input (isopotential point) is 7 pH.

Water molecules in the glass surface are essential for the proton transfer to occur. Non-hygroscopic glasses such as Pyrex and quartz show no pH response. Glasses that can absorb water but have lost their gel layer from contact with non-aqueous and highly acidic or basic solutions or from long-term exposure to air will lose their pH response. It takes about 12 hours of immersion in water to replenish a completely dehydrated layer.



The time that glass electrodes are left dry or exposed to high and low pH solutions must be minimized to maximize the life of the hydrated gel layer.

Instead of a sharp transition between the gel and dry layers, there is continuous decrease in the number of hydronium ions and an increase in the number of lithium or sodium ions from the surface to the interior of glass. As the electrode ages, the outside surface is stripped away and the gel layer penetrates deeper into the glass. Eventually there is a complete breakdown of the silicon oxygen network that forms the glass matrix [Ref. 4.1]. For ideal conditions, (25 °C and zero ionic strength solutions between 6 and 8 pH), a satisfactory glass response should last 2 to 3 years. Most of the variation in life expectancy for these conditions is associated with the manufacturing tolerances with the greatest variability shown for manual glass blowing and assembly. Chemical attack from strong alkaline and acidic solutions, high temperatures, and non-aqueous solutions greatly accelerate corrosion and depletion of the gel layer. The decrease in the electrode efficiency (slope of the millivolt versus pH plot) during the aging process is usually quite moderate (<5%) until a complete loss of the response (zero efficiency and slope) occurs.

The accuracy and precision attainable with pH electrodes in a commercial laboratory environment is much better than what is seen in the field. From an accuracy standpoint, the primary concern is drift or bias developed over time. When pH electrodes are calibrated, the calibration line is characterized by a slope and an asymmetry potential. The asymmetry potential is defined as the potential when the external solution is at pH 7



and 25 °C. While the slope represents the pH responsiveness of the glass, the asymmetry potential represents all the remaining deviations from ideality in both the measurement and reference electrodes. The drift in asymmetry potential for a standard set of electrodes sitting in a buffer solution under ideal conditions in an environmentally controlled laboratory is about 0.002 pH units per day [Ref. 4.4]. Tests for drift should be done with acidic buffers, since the actual pH of basic buffers exposed to air would be continually dropping from the absorption of carbon dioxide. It is difficult in practice to sort out the drift of the electrode from changes in the solution pH.

In regards to precision, the short-term repeatability (same conditions or equipment) for a standard set of electrodes in mild process solutions is about  $\pm 0.01$  pH. Reproducibility (different conditions or equipment) is usually in the range of 0.03–0.04 pH [Ref. 4.4]. Repeatability is the spread in readings for repeated tests in the same solution when a pH is approached from the same direction, whereas reproducibility is the spread in readings at any given pH regardless of time, direction, and solution and includes drift.



**Most accuracy statements and tests are for short-term exposure in a commercial laboratory environment.**

Installation effects, such as variable glass surface conditions, temperatures, ionic strengths, dissociation constants, streaming potentials, concentration gradients, and diffusion or liquid junction potentials cause the pH measurement error in process applications to be an order of magnitude larger than the normally stated accuracy, which is really for electrodes sitting in buffer solutions at laboratory conditions [Ref. 4.5]. Even under the best of industrial conditions (e.g., dilute low ionic strength solutions of weak acids and weak bases between 4 and 10 pH at constant temperature), the long term accuracy even with weekly calibration checks (average bias from lab over a month of operation) is rarely better than  $\pm 0.05$  pH.



**The long-term error of pH measurements installed in the process is an order of magnitude greater than the error normally stated in the literature.**



While the measured and controlled variable is pH, the actual process variable is hydrogen ion activity, which in turn is an indication of reagent concentration. Thus, the effect of mixing equipment and the reagent valve is first on the abscissa (X axis) of the titration curve. The slope of the curve at operating conditions gives the sensitivity of the pH measurement as an inference of process concentrations. For pH system analysis, the abscissa is expressed in terms of a ratio of reagent to feed mass flows for continuous or fed-batch operation and reagent to vessel mass (reagent weight fraction) for traditional sequential batch operation. For the following discussion, we will simplify this to percent reagent flow similar to what is done in Chapter 8 for linear reagent demand control. To really understand what is truly happening in a pH system, one must pay attention to the slope of the titration curve at operating conditions. For example, the slope at 5 and 7 pH may well be 0.05 and 5 pH per percent reagent valve capacity, respectively, for the final stage of a strong acid and strong base system. This means a 0.2% reagent valve stick-slip oscillation translates to a 0.01 and 1 pH amplitude oscillation at the set points of 5 and 7 pH, respectively. Conversely, a 0.1 pH electrode error corresponds to a reagent delivery error of 2% and 0.02% (concentration error) at the set points of 5 and 7 pH, respectively. Furthermore, for a mixing uniformity of 99.9% (standard deviation of 0.1%), the pH fluctuation (noise) would be 0.005 and 0.5 pH at the set points of 5 and 7 pH, respectively.

Measurements on the steep slopes of titration curves will show an extreme sensitivity to concentration fluctuations. Vessels that are well mixed by conventional definitions can introduce 0.1 pH or larger amplitude noise into the measurement. Signal filtering is effective at filtering the high frequency noise in pipelines but not the low frequency non-uniformity in vessels. For strong acid and strong base systems, the steepness of the curve near the neutral point results in a reagent delivery error from the measurement error even with noise that is generally less than the reagent delivery error from stick-slip.

Studies on mixing requirements are typically done on buffered systems or on the tails of the titration curve where the slope is relatively flat. Here, concentration gradients contribute much less to the variability in the measurement so these measurements appear to be more accurate. While the measurement error looks better on a flat curve because of less noise, the corresponding reagent delivery error is actually worse. The reagent delivery for any measurement error is larger and the susceptibility of the glass gel layer and reference process junction to penetration from high concentrations is greater. The reagent delivery error from measurement error is larger than the reagent delivery error from a stick-slip limit cycle that occurs for all PI or PID controllers in automatic. The fact that the measurement error is larger than the control error, means that the use of Coriolis flowmeters and mass ratio control might be better than pH



control in reactors since the concentration of reactants have tight specifications. For neutralization systems and feeds with variable concentrations, pH control remains the best solution.



**The pH measurement error may look smaller on the flatter portion of a titration curve but the associated reagent delivery error is larger.**

Optimistic users and suppliers who provide one electrode per point in the process may believe they have achieved an accuracy of 0.02 pH or better. Results of installations with three electrodes per point in the process show that the error band from mixing noise and reference electrode drift over one a month is at best 0.02 to 0.1 pH for a flat titration curve and 0.2 to 0.5 for a steep titration curve. If all three electrodes agree continually within 0.01 pH for more than a few hours in an industrial application, it indicates that all of the electrodes are either coated, broken, or still have on protective caps [Ref. 4.5 and 4.6].

The maintenance practice of removal and buffering of electrodes is costly and often counterproductive because it reduces measurement accuracy due to damage of the gel surface of the glass electrode, and the upset to the thermal and ionic equilibrium of the reference electrode. It is possible to improve the performance of pH electrodes and safety during pH maintenance and reduce the cost of pH maintenance by an order of magnitude through more realistic expectation, and the use of a better calibration policy that uses process standardization and relaxed tolerances, described in section 4-9.



**The cost of pH measurement maintenance can be reduced by a factor of ten by more realistic expectations and calibration policies.**

Equation 4-1i shows that the potential difference will change at any pH other than 7 if the solution temperature changes. The magnitude of the pH error depends on both the magnitude of the temperature error and the deviation of the pH reading from 7 pH. The size of the error is usually relatively small because the change in the process temperature is small compared to the 273.16 in Equation 4-1i used to convert to degrees Kelvin and because the set point of most pH systems is near the neutral point (7 pH).

The actual pH of the solution changes due to the change in dissociation constants of the ions with temperature. Until recently, compensation of only the change in millivolts generated per pH unit or, in other words, electrode temperature compensation was offered. Microprocessor based transmitters and receivers now offer solution temperature compensation. However, the relationship depends on the composition and operating conditions of the process stream. For strong base streams above 8 pH, the change is often about  $-0.3$  pH per  $10^{\circ}\text{C}$ . Samples that cool down before measurement in the lab will indicate a higher pH than the electrodes installed in the process.

The potential of interest in pH measurement is the difference between the potential developed at the outer and inner glass surfaces of the measurement electrode as defined by Equation 4-1g. All other potential represents an error. Figure 4-1a shows the physical location of the potential ( $E_1 - E_2$ ) and many extraneous potentials for a combination double junction electrode, which has a reference electrode as a concentric ring around the glass measurement electrode. The combination electrode is popular because it reduces the installation and spare parts requirements. The internal salt bridge between the outer and inner junction of the double junction increases the time it takes for process ions to migrate to the inner chamber where the internal silver/silver chloride electrode is located.

$$E_i = E_1 - E_2 - E_3 + E_4 + E_5 - I_i * (R_1 + R_2 + R_5 + R_6 + R_8) \quad (4-1j)$$

Normalizing Equation 4-1i for  $25^{\circ}\text{C}$  so that the slope is 59 mV per pH ( $0.1984*298$ ):

$$E_1 - E_2 = 59 * \frac{(T + 273)}{298} * (7.0 - \text{pH}_1) \quad (4-1k)$$

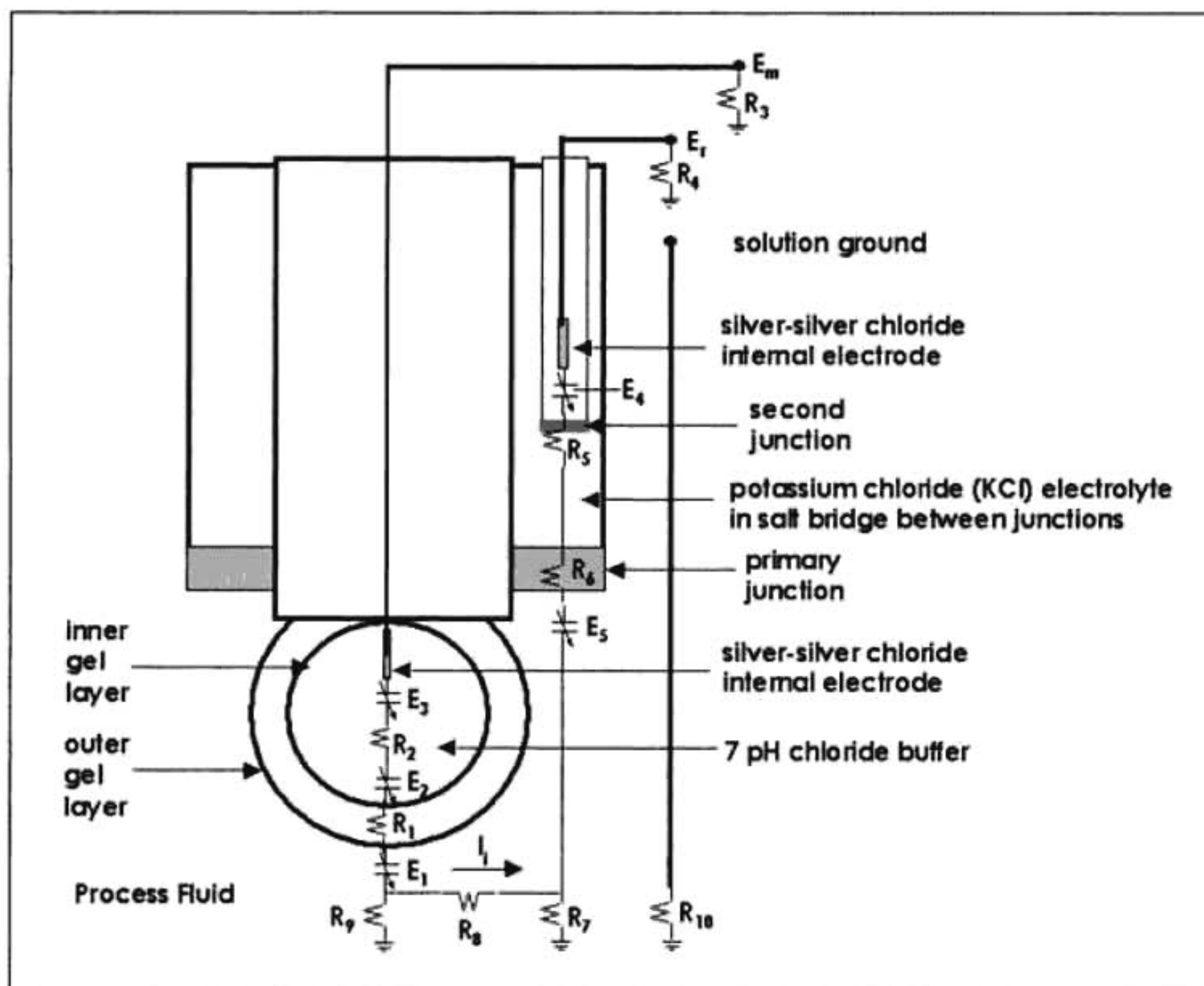
Lumping all the extraneous voltage offsets into one bias voltage:

$$E_{\text{bias}} = -E_3 + E_4 + E_5 - I_i * (R_1 + R_2 + R_5 + R_6 + R_8) \quad (4-1l)$$

Substituting Equations 4-1k and 4-1l into 4-1j, and solving for pH:

$$\text{pH}_1 = 7.0 - \frac{E_i - E_{\text{bias}}}{[59 * (T + 273)/298]} \quad (4-1m)$$





**Figure 4-1a. Equivalent Electrical Schematic of a Double Junction Combination Electrode**

Using digital meter calibration factors with Nernst temperature compensation:

$$pH_1 = pH_{iso} - \frac{E_i - E_{std}}{[(S_{eff}/100\%) * S_{slope} * (T + 273)/298]} \quad (4-1n)$$

Adding solution temperature compensation:

$$pH_{25^{\circ}C} = pH_1 + K_1 * (T - T_{ref}) + K_2 * (T - T_{ref})^2 \quad (4-10)$$

Adding digital transmitter calibration factors to transmit a controlled variable in %:

$$CV_{\%} = \frac{pH_{25^{\circ}C} - pH_{0\%}}{pH_{100\%} - pH_{0\%}} * 100\% \quad (4-1p)$$

Some digital transmitters have a pH span adjustment defined as follows:

$$\text{pH}_{\text{span}} = \text{pH}_{100\%} - \text{pH}_{0\%} \quad (4-1q)$$

where:

$CV_{\%}$	=	controlled variable for pH controller in % of scale (%)
$E_1$	=	potential developed at external glass surface (millivolts)
$E_2$	=	potential developed at internal glass surface (millivolts)
$E_3$	=	half-cell potential at the measurement internal electrode of the (millivolts)
$E_4$	=	half-cell potential at the reference internal electrode (millivolts)
$E_5$	=	liquid junction (diffusion) potential of the reference electrode (millivolts)
$E_{bias}$	=	asymmetry and offset voltages lumped as one bias voltage (millivolts)
$E_{std}$	=	electrode standardization potential (millivolts)
$K_1$	=	solution temperature compensation first order correction factor (pH per °C)
$K_2$	=	solution temperature compensation second order correction factor (pH per °C)
$I_i$	=	input leakage current of the preamplifier (milliamps)
$pH_{iso}$	=	isopotential point (point of zero temperature effect) (pH)
$pH_1$	=	pH at tip of electrode (pH)
$pH_{25^{\circ}C}$	=	pH referenced back to pH at 25°C (pH)
$pH_{span}$	=	pH span for calibration of digital transmitter's output (pH)
$pH_{0\%}$	=	pH at 0% of scale for calibration of digital transmitter's output (pH)
$pH_{100\%}$	=	pH at 100% of scale for calibration of digital transmitter's output (pH)
$R_1$	=	measurement electrode glass resistance (ohms)
$R_2$	=	measurement electrode internal fill resistance (ohms)
$R_3$	=	measurement electrode cable insulation and connection resistance (ohms)
$R_4$	=	reference electrode cable insulation and connection resistance (ohms)
$R_5$	=	reference electrode internal fill resistance (ohms)
$R_6$	=	reference electrode liquid junction resistance (ohms)
$R_7$	=	resistance to ground at measurement electrode tip (ohms)
$R_8$	=	solution resistance between measurement and reference electrode (ohms)
$R_9$	=	resistance to ground at reference electrode tip (ohms)
$S_{eff}$	=	electrode efficiency (%)
$S_{slope}$	=	electrode slope at 25°C (mV per pH) (e.g., 59 mV per pH)
$T$	=	temperature at measurement electrode tip (°C)
$T_{ref}$	=	temperature reference point for solution temperature compensation (°C)

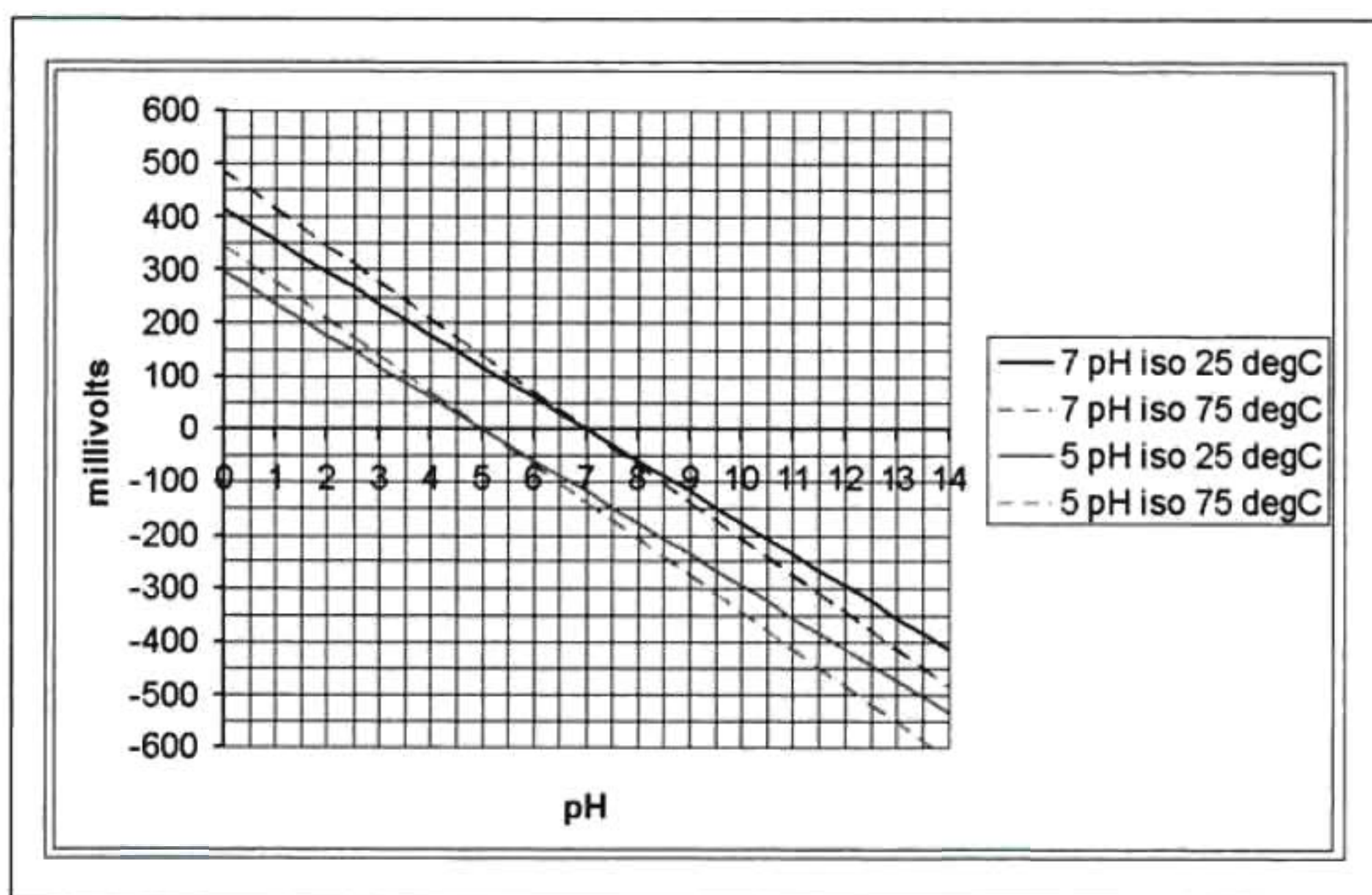
Equation 4-1j shows that the effect of these potentials is additive. Whereas errors from changes in the parameters in Equations 4-1b and 4-1d result in horizontal shifts of the isopotential point as shown in Figure 4-1b, the



extraneous potentials in Equation 4-1j result in a vertical shift of the isopotential point as shown in Figure 4-1c. There is usually no attempt to distinguish and compensate for a shift in the isopotential point that is horizontal from changes in the condition of the gel layer versus a shift that is vertical from changes in the path resistance and condition of the reference electrode.



**Horizontal shifts of the isopotential point from changes in the activity and composition of the gel layer are often unidentified or uncorrected.**



**Figure 4-1b. Changes in the Glass Measurement Electrode cause a Horizontal Shift of the Isopotential Point**

The measurement and reference electrode half-cell potentials in Equation 4-1j, which originate from an electrochemical reaction between the internal electrode element and fill, are of opposite sign and should ideally be equal so that their sum is zero. However, the half-cell potentials depend on the type of internal electrode, the internal fill concentration, and the electrode temperature. If the internal electrode element and fill are identical for the measurement and reference electrodes, then the change in half-cell potential with temperature will cancel out unless a temperature gradient exists. The measurement electrode normally has a silver-silver chloride internal electrode in a chloride buffer. The most common type of reference electrode also has a silver-silver chloride internal electrode and a



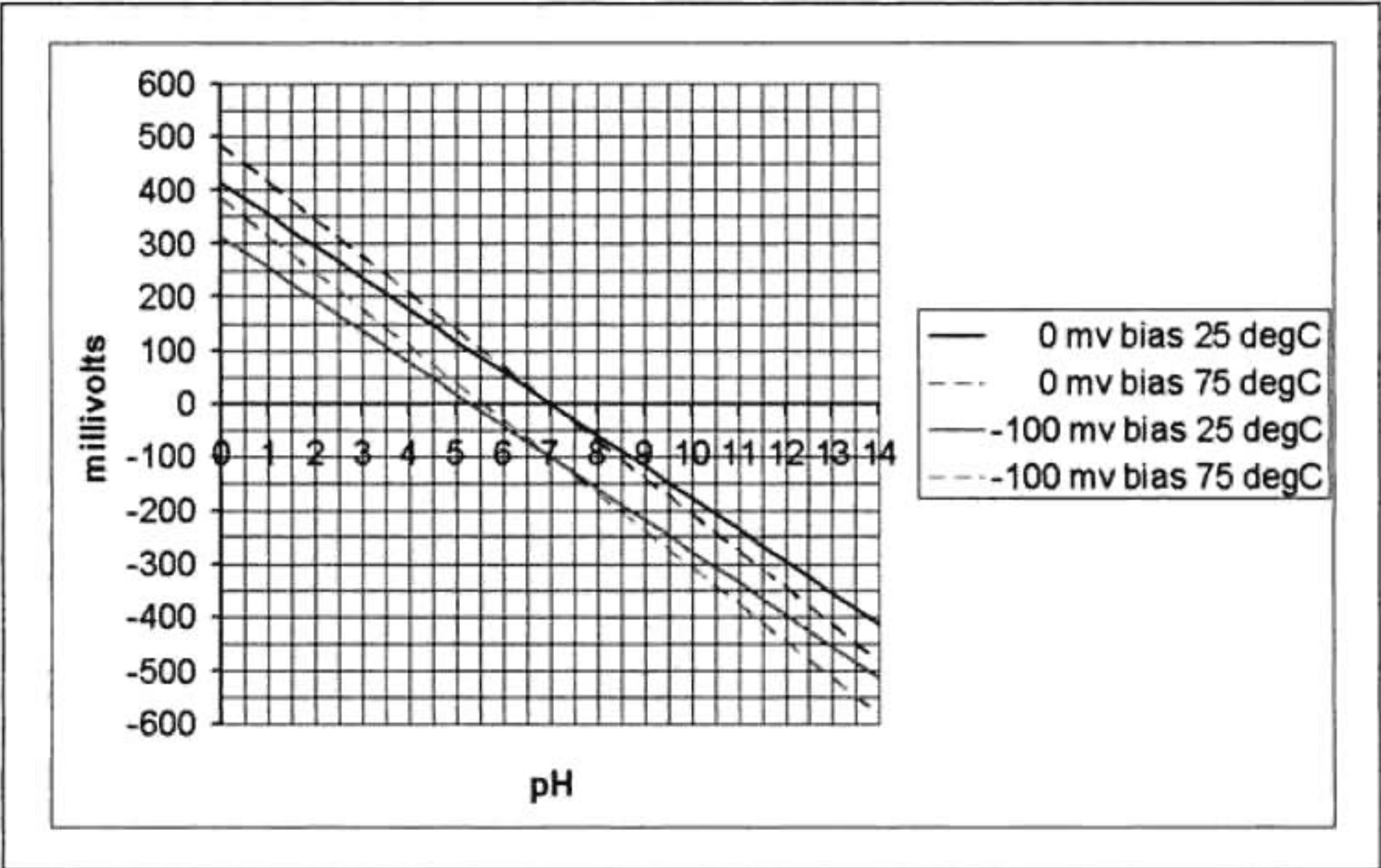


Figure 4-1c. Changes in the Reference Electrode and Path Resistance cause a Vertical Shift of the Isopotential Point

potassium chloride electrolyte. The half-cell potential for a saturated silver chloride electrode ranges from 193 mV at 40°C to 237 mV at 0°C.

Some of the resistances in Equation 4-1j are large. Fortunately, the input leakage current ( $I_i$ ) that flows through these resistances and the amplifier input is extremely small (about 1 picoamp or one trillionth of a milliamp). The current flows from the positive measurement electrode terminal to the negative reference electrode terminal so that the sign of the potential drop is negative compared to the measurement electrode's outer potential and consequently causes the isopotential point to shift down and the pH measurement to go upscale.

The measurement electrode glass bulb resistance is normally the largest resistance. It ranges from about 20 Mohms to 500 Mohms at 25°C depending on the type and thickness of the glass. Rugged glasses that are thicker than normal for greater resistance to breakage and abrasion and a longer life in terms of time to failure of the silicon oxide matrix from penetration of the gel layer, often have a lower resistance per unit thickness so that the increase in total resistance is moderated. The resistance dramatically increases at low temperature and can exceed 1000 Mohms if the E-type glass shown in Figure 4-2a is used that is normally reserved for concentrated acidic solutions at high temperatures. Since a greater electrical resistance per unit thickness normally translates to a greater resistance to etching and high temperatures, rugged electrodes are not generally suitable for hot alkaline solutions. However, advances are



continually being made in glass formulations that increase the range of permissible operating conditions. Equation 4-1q quantifies the exponential increase in resistance with temperature.

$$R_{m1} = R_{m0} * 10^{-K_{exp} * (T_1 - T_0)} \quad (4-1r)$$

where:

$K_{exp}$  = exponential factor for glass type (e.g., 0.04)

$R_{m1}$  = resistance at temperature at  $T_1$  (ohms)

$R_{m0}$  = resistance at temperature at  $T_0$  (ohms)

$T_1$  = process temperature 1 ( $^{\circ}\text{C}$ )

$T_0$  = process temperature 0 ( $^{\circ}\text{C}$ )

The first stage amplifier should have an input resistance that is 1000 times greater than the total resistance of the path from the measurement electrode through the reference electrode so that the IR drop through the amplifier is insignificant. The connection and insulation resistance of the measurement electrode cable should be at least 100 times greater than the path resistance to insure that the parallel resistance to ground ( $R_3$ ) at the measurement input to the Field Effect Transistor (FET) amplifier has a negligible effect.



**The glass electrode requires exceptional cable insulation and amplifier input resistance and connection integrity to reduce measurement noise.**

Dehydration of the glass electrode can cause a significant increase in its resistance ( $R_1$ ). However, the gradual penetration of the gel layer into the interior of glass and thinning of the dry glass from the aging process or chemical attack should show up as a decrease in electrical resistance.

Measurement electrodes whose surface is coated will have a higher resistance ( $R_1$ ) but the percentage increase is usually small and difficult to detect, particularly since the glass resistance is an exponential function of temperature per Equation 4-1q. Coatings are best detected as a dramatic increase in the time constant of the electrode since thin almost imperceptible coatings greatly slow down the migration of hydronium ions. For example, a 1 mm coating on the glass can increase the response time (time to reach 98% of the final response) of the glass electrode from 10 seconds to 7 minutes [Ref. 4.7].

The reference electrode junction resistance is normally only 1 to 10 kohms. The onset of a coating or partial plugging of the porous junction can easily



**The onset of a coating of the glass measurement electrode shows up as a large increase in its time constant and response time.**

cause the resistance ( $R_6$ ) to more than double. However, salts from the process precipitating in the junction will be highly conductive and will not show up as an increase in resistance.



**The onset of a non-conductive coating of the reference electrode shows up as a large increase in its electrical resistance.**

The resistances of the internal electrode fills and external process fluid are normally only a few thousand ohms so that the potential drop due to leakage current flow is negligible. However, high purity water (i.e., distilled water, de-ionized water or steam condensate) and non-aqueous solutions have an extremely high resistance ( $R_8$ ) that approaches the resistance ( $R_1$ ) of the glass.

A high total electrical resistance from applications with high resistance glass at low temperatures ( $< 20^\circ\text{C}$ ), dehydrated glass, or in non-aqueous and pure water streams cause the pH measurement to be sluggish and more susceptible to noise from ground paths, streaming potentials (static electricity), fluid velocity, and electrical interference.



**Non-aqueous and pure water streams require extra attention to shielding and process path length and velocity to minimize pH measurement noise.**

Ions migrate from areas of high to low concentration by diffusion. As ions move into the porous junction of the reference electrode, they establish a voltage known as the “liquid junction potential” or “diffusion potential” ( $E_5$ ). The more mobile ions accumulate in the junction faster and build up an excess charge that slows down the further accumulation of these ions. The potential  $E_5$  and consequently the pH reading shifts until an equilibrium is reached. The potential  $E_5$  for the standard KCl reference electrolyte is relatively small because the potassium ( $\text{K}^+$ ) and chloride ( $\text{Cl}^-$ ) ions electrolyte have about the same mobility, which means they accumulate in the junction at about the same rate. However, a KCl electrolyte is not normally used in process fluids with compounds such as



sulfides and nitrates that cause the formation of precipitates that clog the junction.

A more common problem is the migration of process ions into the reference junction. Again, an excess charge of the more mobile ions accumulates until an equilibrium is reached that slows down the faster ions. The final potential  $E_5$  established from the migration of ions into the junction can be estimated by the Henderson Equation 4-1r, which shows that the potential increases with the difference in the mobility of the positive and negative ions and the concentration of ions in the electrolyte and process solution [Ref. 4.2]. Thus, low and high ionic strength process solutions create a high junction potential.

$$E_5 = \frac{(I_{p+} - I_{p-}) - (I_{e+} - I_{e-})}{(E_{p+} + E_{p-}) - (E_{e+} + E_{e-})} * \frac{R * (T + 273.16)}{F} * \ln \left[ \frac{(E_{p+} + E_{p-})}{(E_{e+} + E_{e-})} \right] \quad (4-1s)$$

$$E_{e+} = \sum (c_{ei+} * \mu_{ei+} * z_{ei+}) \quad (4-1t)$$

$$E_{e-} = \sum (c_{ei-} * \mu_{ei-} * z_{ei-}) \quad (4-1u)$$

$$E_{p+} = \sum (c_{pi+} * \mu_{pi+} * z_{pi+}) \quad (4-1v)$$

$$E_{p-} = \sum (c_{pi-} * \mu_{pi-} * z_{pi-}) \quad (4-1w)$$

$$I_{e+} = \sum (c_{ei+} * \mu_{ei+}) \quad (4-1x)$$

$$I_{e-} = \sum (c_{ei-} * \mu_{ei-}) \quad (4-1y)$$

$$I_{p+} = \sum (c_{pi+} * \mu_{pi+}) \quad (4-1z)$$

$$I_{p-} = \sum (c_{pi-} * \mu_{pi-}) \quad (4-1aa)$$

where:

$c_{ei+}$  = concentration of positive ion species  $i$  in the electrolyte

$c_{ei-}$  = concentration of negative ion species  $i$  in the electrolyte

$c_{pi+}$  = concentration of positive ion species  $i$  in the process

$c_{pi-}$  = concentration of negative ion species  $i$  in the process

$E_5$  = liquid junction (diffusion) potential of the reference electrode

$E_{e+}$  = accumulated charge of positive ions from the electrolyte in the junction

$E_{e-}$  = accumulated charge of negative ions from the electrolyte in the junction

$E_{p+}$  = accumulated charge of positive ions from the process in the junction

$E_{p-}$	=	accumulated charge of negative ions from the process in the junction
$F$	=	Faraday Constant (94487 C/ mol, C is an abbreviation for coulomb)
$I_{e+}$	=	accumulated concentration of positive ions from the electrolyte in the junction
$I_{e-}$	=	accumulated concentration of negative ions from the electrolyte in the junction
$I_{p+}$	=	accumulated concentration of positive ions from the process in the junction
$I_{p-}$	=	accumulated concentration of negative ions from the process in the junction
$\mu_{ei+}$	=	mobility of positive ion species i in the electrolyte
$\mu_{ei-}$	=	mobility of negative ion species i in the electrolyte
$\mu_{pi+}$	=	mobility of positive ion species i in the process
$\mu_{pi-}$	=	mobility of negative ion species i in the process
$R$	=	Ideal Gas Constant (8.314 J/ mol*K)
$T$	=	solution temperature (°C)
$z_{ei+}$	=	valence (charge) of positive ion species i in the electrolyte
$z_{ei-}$	=	valence (charge) of negative ion species i in the electrolyte
$z_{pi+}$	=	valence (charge) of positive ion species i in the process
$z_{pi-}$	=	valence (charge) of negative ion species i in the process



When "special electrolytes" are selected, there should be virtually no difference in the mobility of their ions, such as potassium nitrate ( $KNO_3$ ).



Extremely dilute or concentrated process streams cause a larger junction potential because the process has a much lower or higher ionic strength respectively, than the reference electrolyte.

The movement of process ions into the reference electrode will also plug its junction and eventually contaminate its internal electrolyte. To reduce the rate of contamination at the internal silver-silver chloride electrode element and the shift of potential  $E_4$ , smaller reference junctions, second internal junctions, gel electrolytes, porous solid internals, and flowing junctions are used. Smaller junctions increase the rate of fractional plugging of the junction and therefore reduce the time to a totally plugged junction. Double junctions, gel electrolytes, and porous solid internals increase the time required for the reference junction potential to reach equilibrium after inserted into a process stream or for a dramatic change



in the stream, which might occur during start-up or during batch operation. Thus, designs seek a compromise between the conflicting needs for a fast, uncontaminated, and unplugged electrode. It is interesting that extremely slow references will ignore short-term fluctuations in stream concentrations from imperfect mixing and may actually appear to provide a more stable (lower noise) reading. Also, if the electrode is only immersed for a relatively short time (1 or 2 minutes) into the process by an automatically retractable assembly, the reference may not have had time to change its potential.



**Reference junctions with large pores and areas decrease the rate of plugging of the junction but increase the rate of contamination of the internals.**



**Double junctions, gel electrolytes, and solidified internals decrease the rate of contamination but increase the time to equilibrium.**



**Slow references may be more stable for short-term fluctuations from imperfect mixing and short exposure times from automated retraction.**

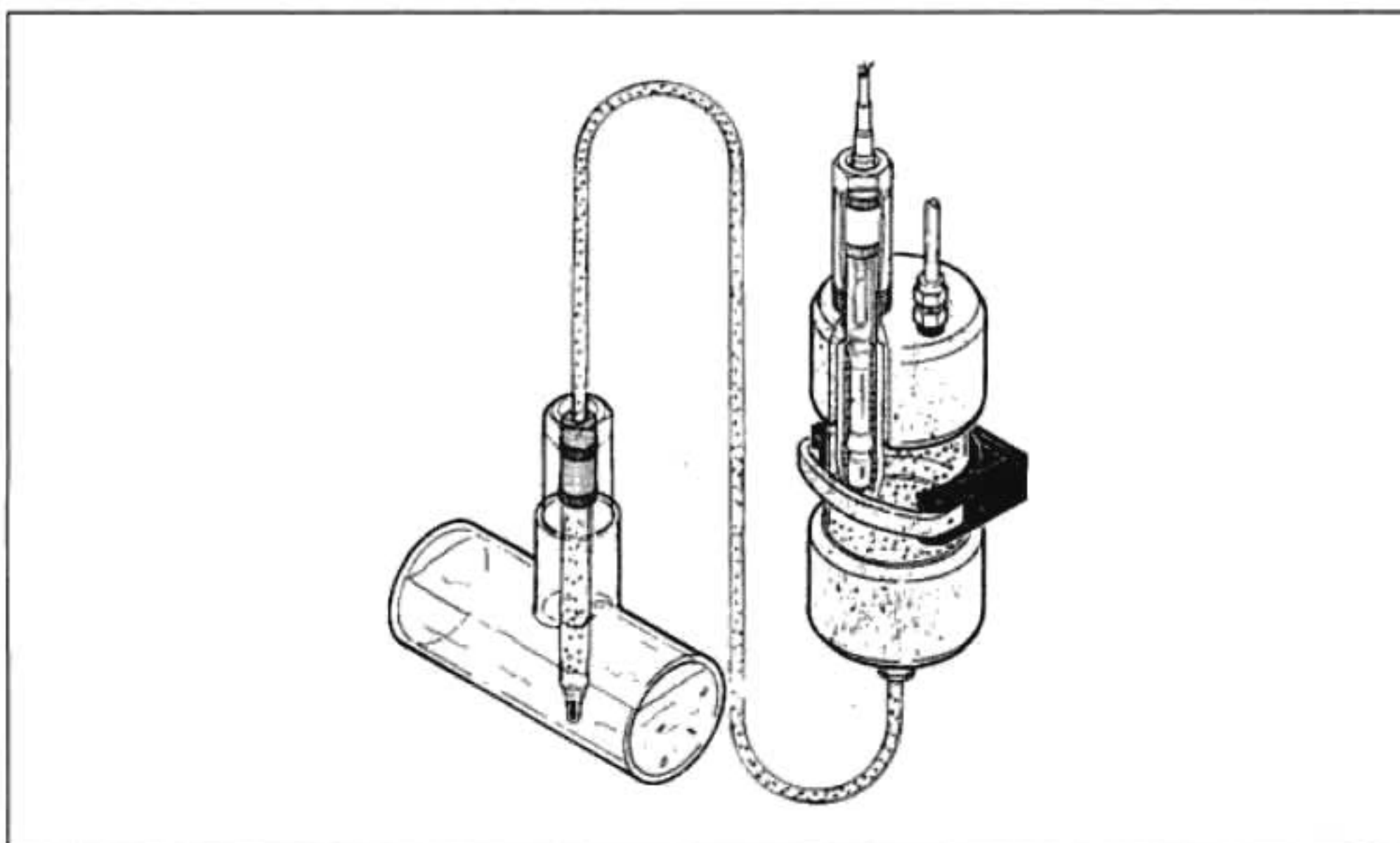
Solid references with small pore sizes help prevent the movement of small process particles into the junction. If this design is combined with an internal helical reference pathway, it is possible to have a large reference junction area to reduce the rate of fractional coating without a detrimental increase in the rate of contamination. However, precipitation reaction of the silver or potassium electrolyte can rapidly occlude the small pores so these electrodes should not be exposed to cyanides, bromides, iodides, sulfides, or nitrates. Methods to immobilize the electrolyte are used to reduce the migration rate of the electrolyte ions into the junction thereby extending the life of the reference and decreasing the rate at which the reference potential changes.

The fastest and most accurate reference electrode has a flowing junction. A constant small flow of electrolyte purges the junction and prevents movement of the process into the junction. The result is a small quickly established liquid junction potential that can meet the demands of high accuracy and batch applications. However, the reference flow must be kept small enough so as to not contaminate the process or excessively

deplete the electrolyte by pressurizing the reservoir to maintain an appropriate pressure differential between it and the process. The external salt bridge shown in Figure 4-1d provides the ultimate isolation of the reference's internal half cell from the process. The additional installation and maintenance cost of this external pressurized reservoir makes this an unpopular choice with technicians, unless it can be translated into reduced probe calibration and replacement or recognized process benefits from reduced variability.



**The fastest and most accurate reference has a flowing junction but it requires regulated pressurization to maintain a small positive electrolyte flow.**



**Figure 4-1d. Ultimate Protection against Contamination by an External Salt Bridge (Courtesy of Yokogawa)**

## 4-2. Measurement Electrodes

A large surface area spherical glass bulb measurement and flowing junction reference electrode has the best accuracy because it has the fastest and lowest resistance glass and reference junction with the fewest extraneous potentials. A separate temperature probe also provides the fastest compensation for changes in process temperature. However, a flowing reference electrode requires pressurization and periodic filling of the reservoir. Additionally, the accuracy and speed of response is only obtained with glass surfaces and reference junctions that are free from



contamination, abrasion, and coatings. Also, compared to the combination electrode there are now three times as many electrodes to install, maintain, and troubleshoot and the glass bulb may have an unacceptable life expectancy or not be permitted in food processes.



Spherical glass bulb and flowing reference electrodes offer the most accurate pH measurement but have higher installation and maintenance costs. The lifecycle cost may be less if the value of a smaller pH measurement error is significant and fouling, abrasion, and breakage of the electrodes is not an issue.

Manufacturers generally offer several different glass formulations that are tailored to a meet process requirements. Figures 4-2a, 4-2b, and 4-2c show the electrical resistance, temperature and pH ranges, and the alkalinity error for four types of glasses. Higher glass impedance normally corresponds to a higher resistance to chemical attack from strong bases and strong acids, but progress has been made in reducing the impedance of glasses so that they could be used at lower temperatures.

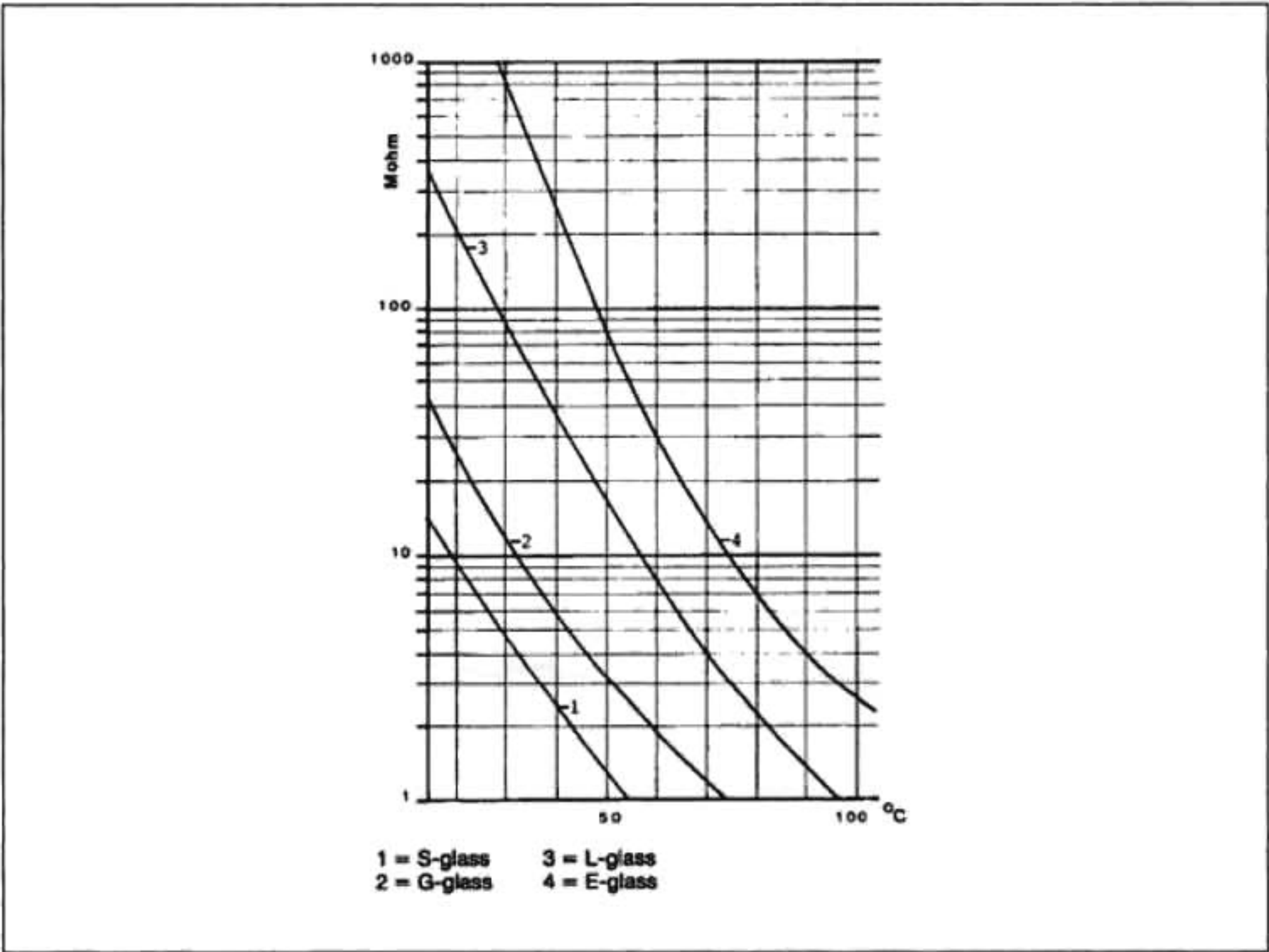


Figure 4-2a. Electrical Resistance of Various Glass Formulations (Courtesy of Yokogawa)

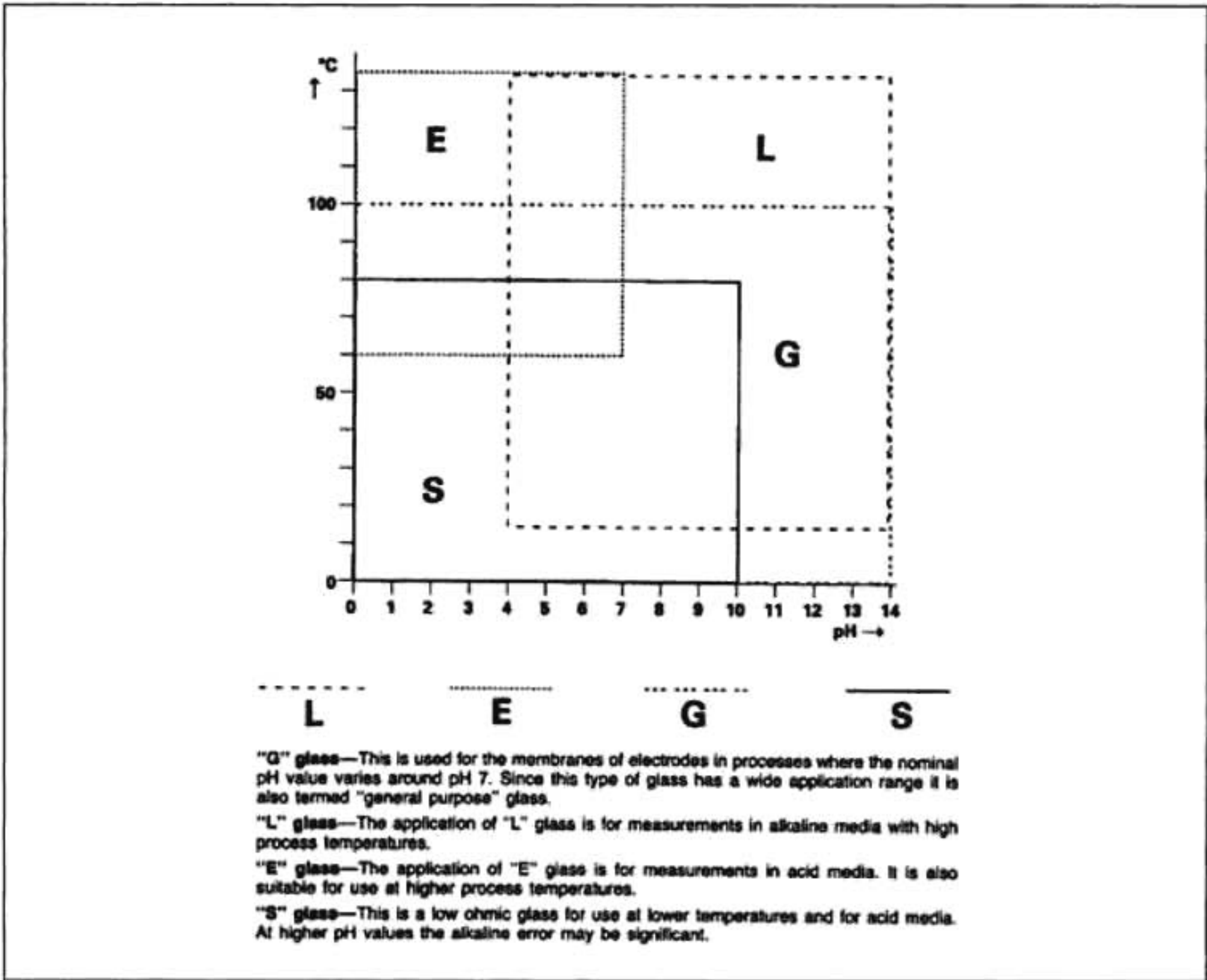


Figure 4-2b. Temperature and pH Range of Various Glass Formulations (Courtesy of Yokogawa)

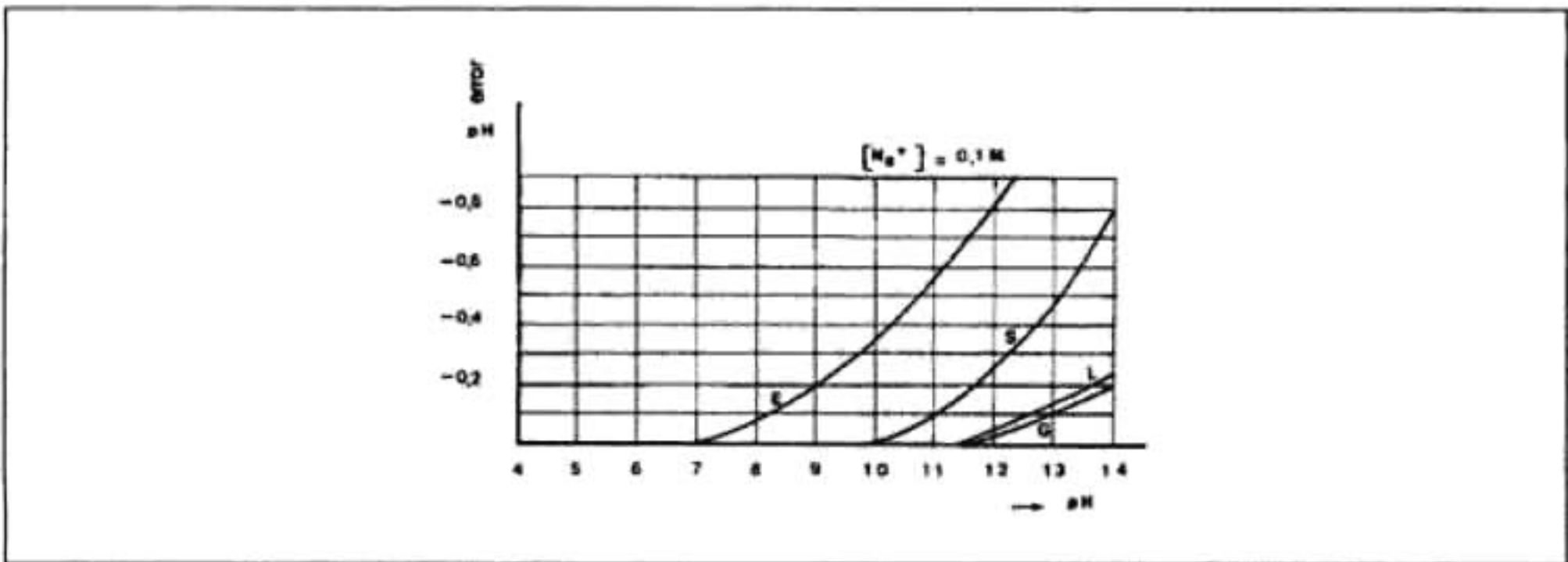
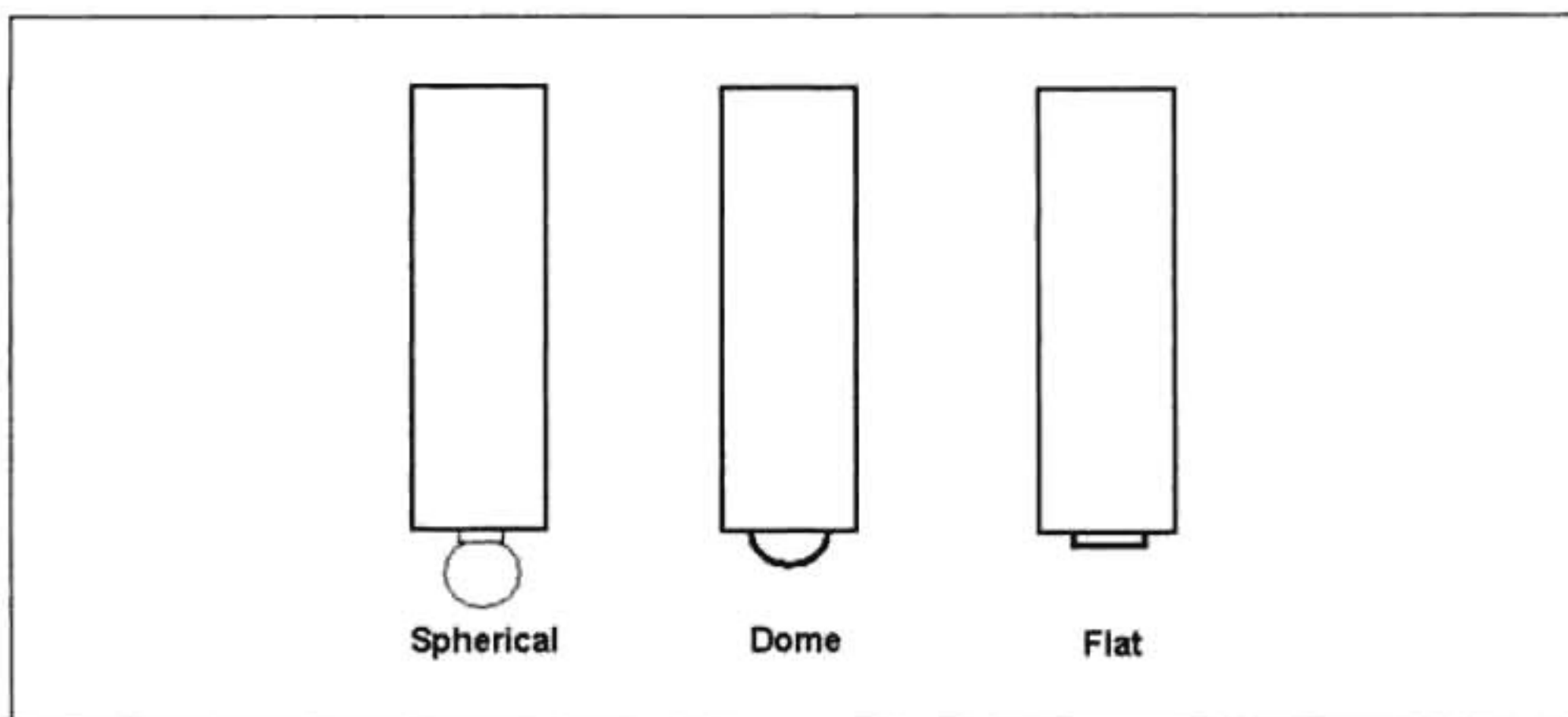


Figure 4-2c. Alkalinity Error of Various Glass Formulations (Courtesy of Yokogawa)

Originally measurement electrodes used a spherical glass bulb design with a 0.2 to 0.5 mm thickness for the pH sensing membrane. Cracks tended to occur at the transition from the bulb to the straight side, although direct impingement of solids or debris caused cracks anywhere on the bulb. Most manufacturers now offer rugged dome and flat glass sensors depicted in Figure 4-2d and ion sensitive field effect transistors (ISFET).





**Figure 4-2d. Spherical Bulb, Rugged Dome, and Flat Glass Sensors**

The prevalent reference electrode in the 1970s had a liquid electrolyte and a flowing junction and was separate from the measurement electrode. In the 1980s, combination electrodes incorporating double reference junctions as shown in Figure 4-1a enabled a throwaway concept by eliminating the need to refill reference solutions or troubleshoot separate electrodes. The electrolyte is made as a gel or saturated in special wood or polymers to reduce the rate of contamination. Reference electrodes with porous solid materials impregnated with electrolyte are often called “solid-state” electrodes. In the 1990s, the pore size was reduced and the junction area increased.

Besides the standard suite of measurement and reference electrodes just mentioned, there are also some special designs intended to address particular application concerns that reduce the life or increase the installation and maintenance costs. Publications typically tout the advantages, and articles document the success stories. However, no electrode is perfect and a compromise is always at play. The following discussion will attempt to provide guidelines and discussion of the tradeoffs based on limited testing, conversations with pH specialists, and application experiences in the 1980s. For much greater detail on the construction of various electrodes, the reader is referred to Reference 4.7. All the electrodes presented here were developed in that time frame although improvements have certainly been made. Before an electrode is used in any difficult or demanding application, it should be installed in the process on a test basis and monitored closely.

Glass domes or hemispheres are used to provide a stronger shape and a thicker glass membrane. These “rugged glass” electrodes are designed to provide a longer life by reducing the chance of cracking during installation and maintenance and from exposure to aggressive fluids where abrasion, etching, or corrosion is a concern. If the dome has a higher

total electrical resistance, it may not be suitable for low temperatures and may exhibit a slower response. If the electrical resistance per unit thickness is reduced to lower the total resistance, the glass may actually be more susceptible to chemical attack.

Flat glass electrodes have been developed to minimize direct impingement to prevent abrasion and maximize a sweeping action to reduce fouling. For viscous fluids, it also eliminates the separation of the flow field and stagnation associated with the downstream side of a spherical bulb. These electrodes generally have a stated range of 2 to 12 pH. Streams with high sodium ion concentrations and ionic strengths have been observed to introduce a greater error for flat glasses. Large flat glass electrodes have been reported to exhibit a significant undocumented and uncompensated temperature effect [Ref. 4.9 and 4.10].

Pfaffler patented a measurement electrode made of Glasteel™, a unique material formed by the fusion of glass and steel with an enamel coating. For operation below 5 pH, the probe has greater structural endurance, corrosion resistance, and a higher temperature rating of 140°C as shown in Figure 4-2e-1. It is designed to withstand the rigors of heat, pressure, and dynamic agitation in acidic reactors. It needs a transmitter that can be calibrated for a zero potential point between 1 and 3 pH. The primary adapter seen in Figure 4-2e-2 provides the solution ground needed by smart transmitters for impedance diagnostics. The Galsteel™ electrode provides a “relative” pH measurement in that the pH value sensed is not the same as that developed from a conventional pH electrode. However, the reproducibility and life expectancy may be better and the life-cycle cost less for reactors despite a much higher initial cost.

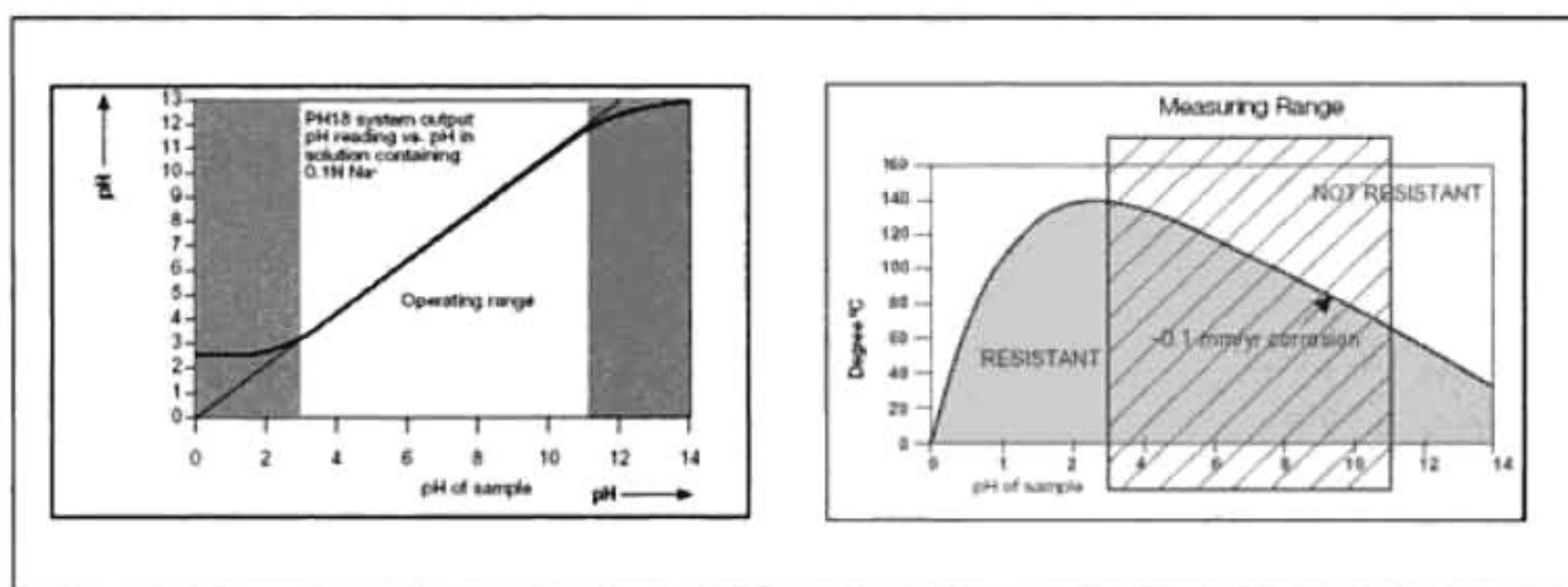
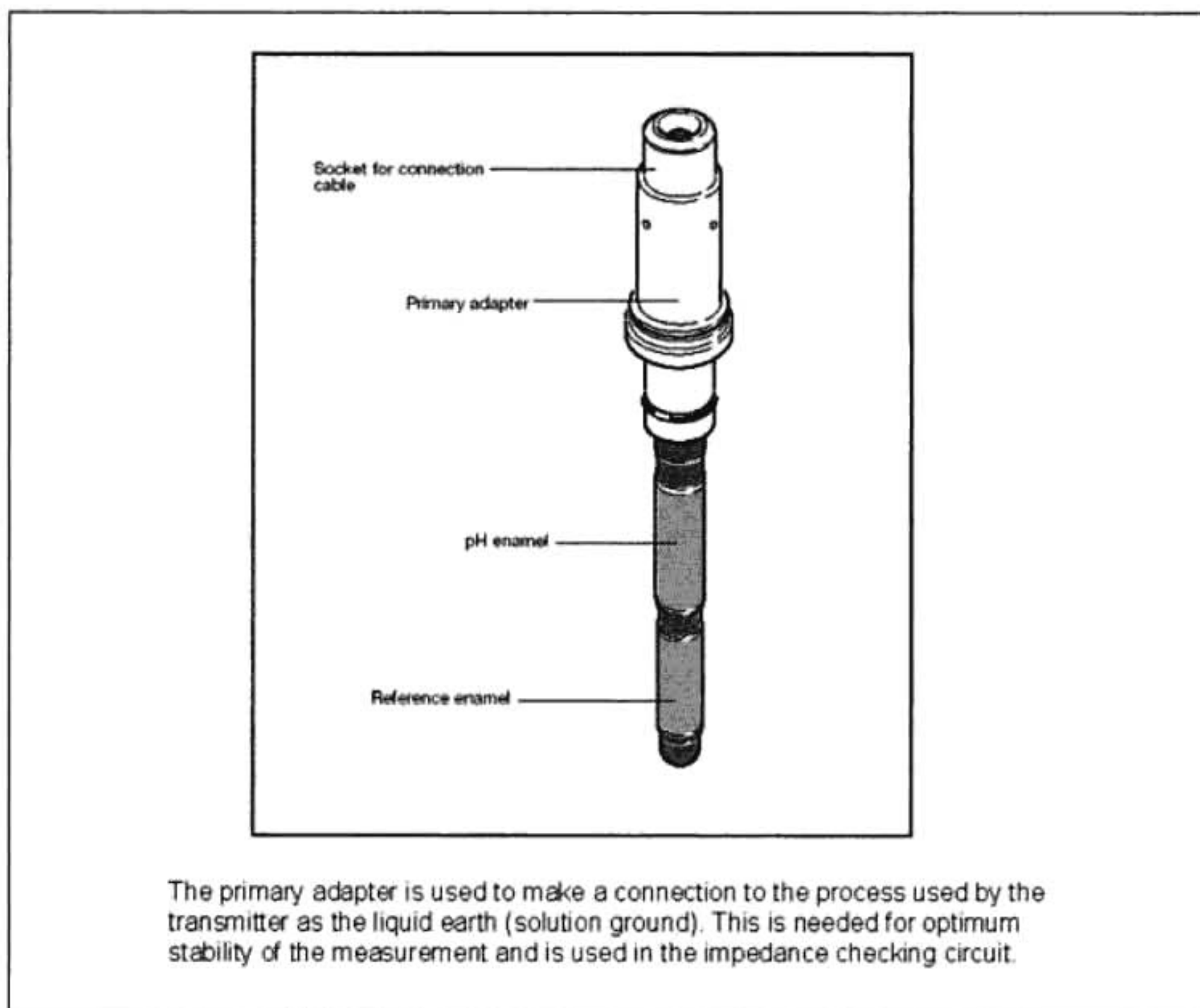


Figure 4-2e-1. Glasteel™ Electrode pH and Temperature Range (Courtesy of Yokogawa)

Before the glass measurement electrode was developed for industrial measurement, an antimony electrode was used. Antimony is a hard, brittle material. The electrode responds by oxidation of its surface. Since oxidant accumulation on its surface deteriorates the accuracy and





**Figure 4-2e-2. Glasteel™ Electrode Installation (Courtesy of Yokogawa)**

repeatability of the measurement, periodic cleaning is necessary. The electrode's response is nonlinear and requires narrow calibration spans or special polynomials for adequate accuracy. It is not recommended for operation below 2 pH. It is more temperature sensitive than the glass electrode. The approximate 50 mV output per pH unit increases from 1 to 3 mV per °C as the pH increases. The isopotential point is about 2 pH so transmitters with an adjustable isopotential point are required for temperature compensation. Finally, antimony is an oxidation reduction potential (ORP) electrode. It responds to oxidizing and reducing species, and its reading will be affected by less than one part per million (ppm) chlorine. Antimony is used as a last resort; applications where abrasion from slurries or etching from hydrofluoric acid causes glass measurement electrode failures. It cannot be used in food beverage, or pharmaceutical applications due to the toxicity of antimony [Ref. 4.10].

Other metal-oxide electrodes have been developed that use a membrane that is designed to permit the migration of hydrogen ions but block the oxidizing and reducing species that are responsible for the ORP effect. Without a sufficiently thick membrane, reducing agents such as ascorbic acid decrease the millivolt potential developed and increase the pH

reading. Oxidizing agents such as hydrochloride have the opposite effect. Increasing the membrane thickness decreases the speed of responses to pH, which already is slow in the neutral region. These electrodes have no installed base and are presented here as areas for further research and development.

Monsanto Company patented an iridium oxide pH probe with a polymer coating that blocks negative ions. The ORP effect from positive ions is slowed down but not eliminated. The electrode requires a modified or microprocessor-based transmitter, because the zero potential point is about 10 pH and the isopotential point is near 4 pH. It generates about 91 mV per pH unit at 25°C. Iridium oxide has better linearity and repeatability than antimony and a potential temperature rating of 200°C. It also eliminates problems of dehydration, etching sodium ions and breakage associated with glass electrodes, and can make measurements outside the 0–14 pH range [Ref. 4.10]. However, a reported drift of 0.1 pH per day would necessitate frequent calibration.

General Electric patented a high temperature pH sensor where a yttria stabilized zirconia tube provides the selective migration of hydrogen ions to an inner copper oxide electrode. The pH sensor has been shown to agree within 0.5 pH of calculated values at 285°C between 3 and 9 pH with uncertainty as to whether the discrepancies were due to the calculation or the measurement. There is no alkalinity error. However, the speed of response of the membrane degrades with time [Ref. 4.11 and 4.12]. The expected life expectancy of a few months and a reported drift of 0.1 pH per day needs investigation.

Leeds & Northrup patented the DURAFET™ pH electrode shown in Figure 4-2f. It uses an ion-sensitive field effect transistor (ISFET) instead of glass to provide a low-impedance, breakage-resistant measurement electrode. This is the electrode of choice when glass is not permitted. The characteristic drift of laboratory versions of ISFET pH sensors has been reduced. It is much faster than glass since the response is by an electrical field rather than by movement of hydrogen ions into a membrane. It has integrated automatic temperature compensation and has no sodium ion error or known ORP interference. It needs no hydration, and uses a conventional reference electrode. The slope of about 59 mV per pH unit is close to that for glass, but the isopotential point shift necessitates a special calibration. The thin silicon nitride crystal covering is susceptible to degradation if faced into the flow. Unlike glass sensors, the ISFET requires no hydration and generally has a longer life if left dry. There has been some discussion but no documentation of the life expectancy in process solutions or the interference from stray electrical fields and ground potentials. Most electrode manufacturers now offer an ISFET pH probe.



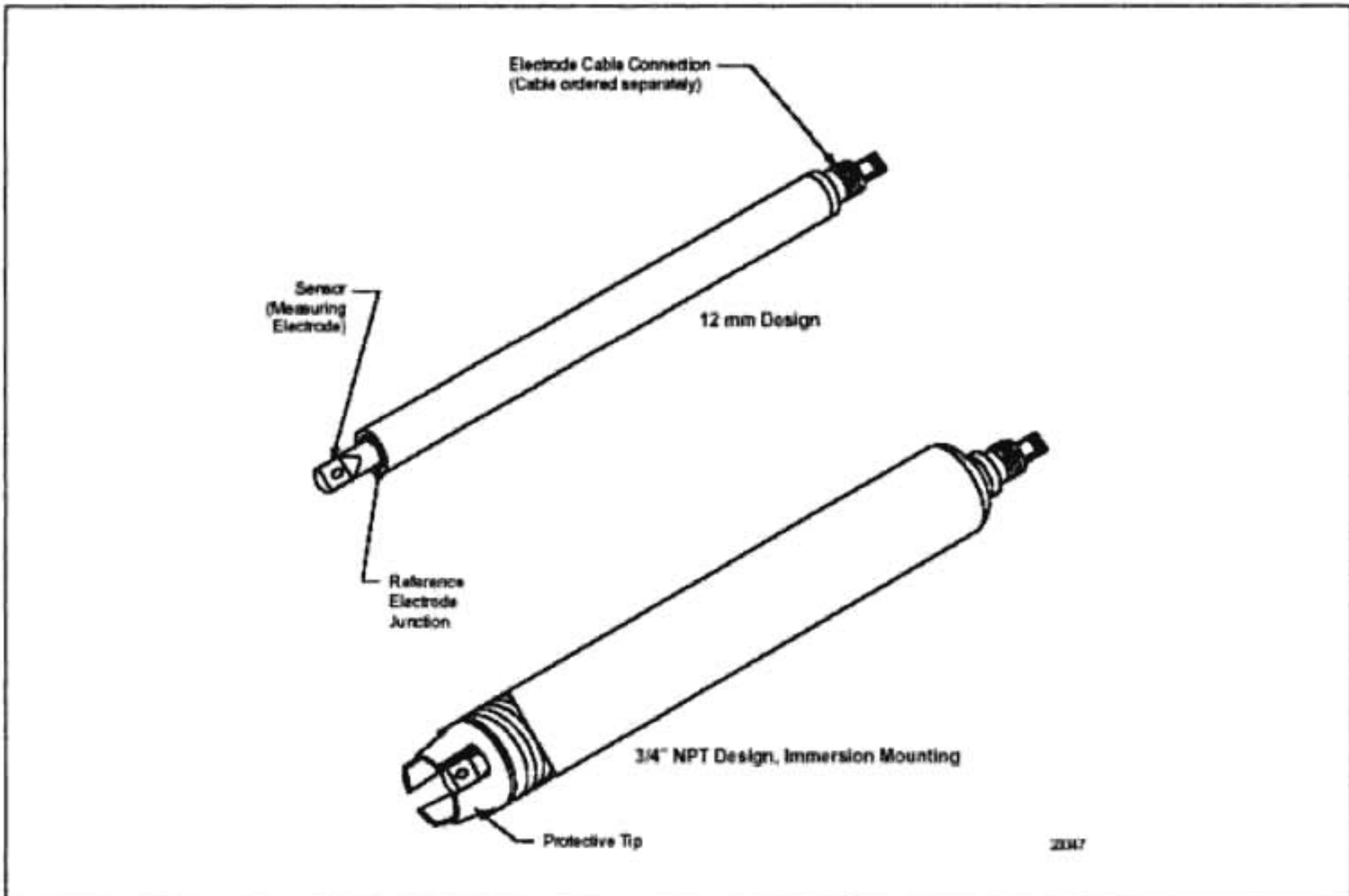
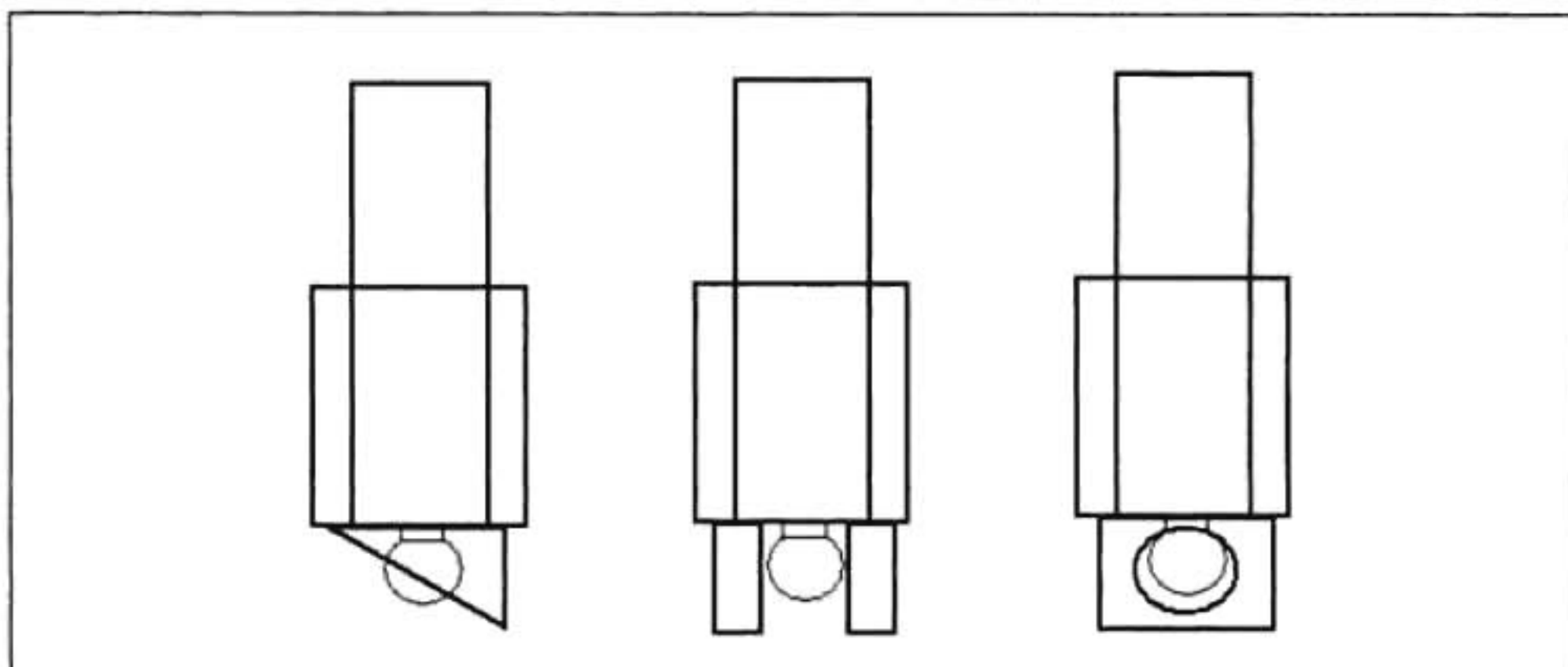


Figure 4-2f. Ion Sensitive Field Effect Transistor (ISFET) Electrode (Courtesy of Honeywell)

Most pH measurement electrodes use glass bulbs with various shroud designs to provide bulb protection (from breakage and abrasion) and bulb exposure to flow (to ensure a representative reading and prevent areas of stagnation and material buildup) as shown in Figure 4-2g. The standard design has slots or holes to allow the process to flow around the bulb. Shrouds where the bulb is recessed without a slot or hole are used for pulp and very abrasive applications. However, the recessed area can become clogged or caked up, covering the bulb and reference junction. When material breaks loose, it can take the bulb with it. A bubble can also get trapped in the shroud. A tapered shroud is favored for coating applications since it creates eddies to help keep the electrode surfaces clean [Ref. 4.8].

### 4-3. Reference Electrodes

The construction features of a particular reference design in a reference electrode present a tradeoff in the effort to quickly establish and minimize a constant junction potential, while resisting contamination and coating. The user must decide which is most important for a given application. A decrease in the area of the reference junction reduces the rate of contamination, but increases the fractional rate of coating and plugging. A thickening or solidification of the internal fill, the addition of double and triple junctions, and a decrease in the junction porosity slows down



**Figure 4-2g. Shroud Designs Work a Compromise between the Needs for Bulb Protection and Bulb Exposure to Flow**

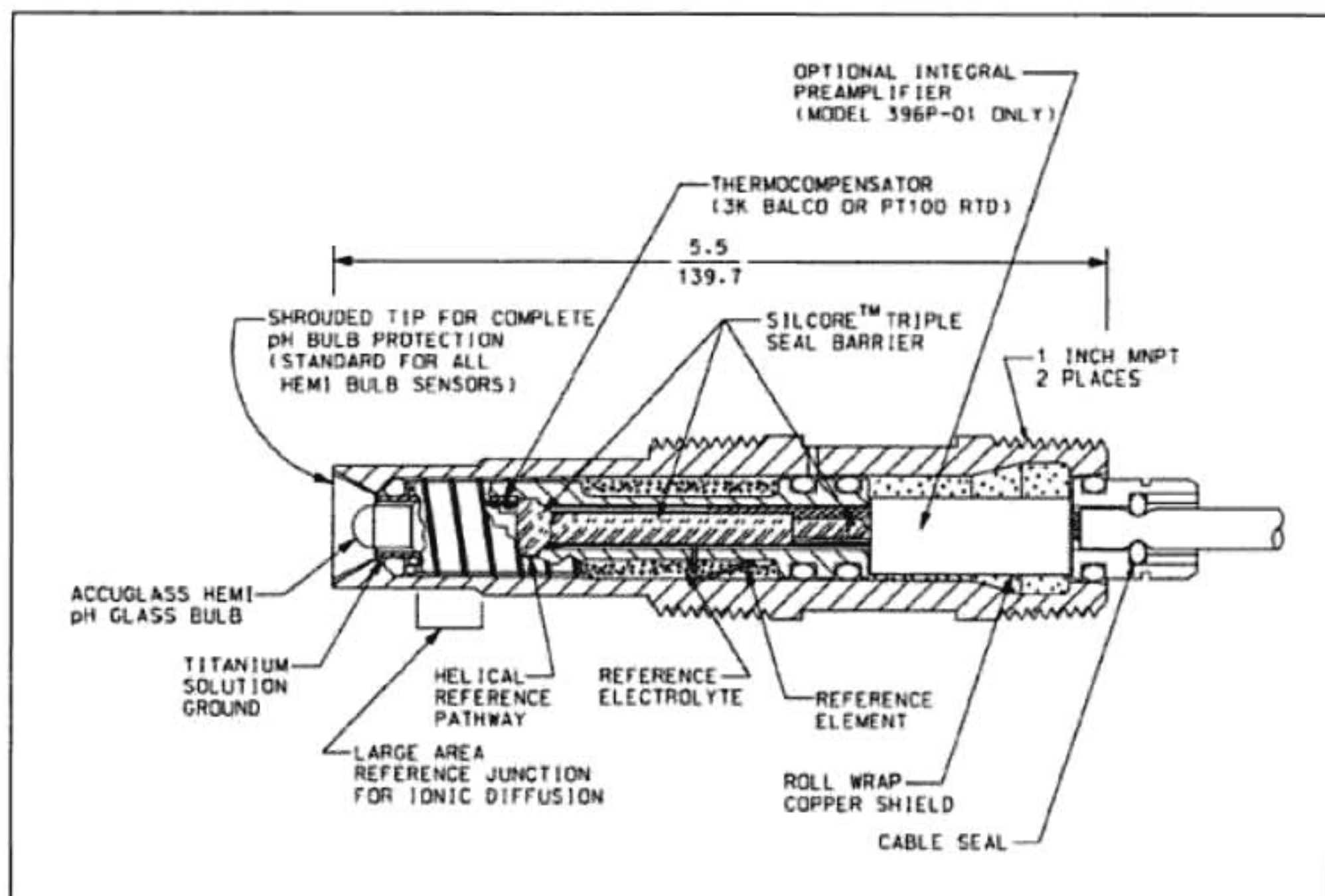
contamination, but delays equilibrium and often increases the magnitude of the junction potential.

The most popular reference electrode has a silver-silver chloride inner electrode and a potassium chloride electrolyte. The potassium and chloride ions have about the same mobility, which minimizes the junction potential from a difference in diffusion rates. However, the potassium chloride solution is saturated and tends to crystallize especially at low temperatures, which reduces the diffusion rate and causes a drift in the associated potential at the junction. Also, silver from the silver-silver chloride internal element gets into the potassium chloride fill, reacts with sulfides and nitrates, and clogs the junction.

Rosemount patented a TUpH<sup>TM</sup> sensor shown in Figure 4-3a that has a solid reference with micron-size helical pathways, a triple seal barrier, and a reference junction that covers the whole lower sleeve area of the combination electrode to resist plugging and contamination. It also uses a new glass formulation with low-sodium ion error that resists breakage especially at high temperatures and protects the electrode from vibration and shock by transferring energy away from the glass-metal seal, which should translate to significantly lower maintenance costs in harsh, hot, caustic, dirty, and abrasive streams. It should not be used where precipitation of the internal electrolyte could plug the small pores or where a rapid reference equilibrium is required.

In 1976, TBI patented a solid-state reference electrode shown in Figure 4-3b that is nearly impervious to process contamination. The reference consists of four wooden dowels saturated with potassium chloride solution. Process material must work its way up into the innermost wooden dowel, where the internal silver-silver chloride element resides to create a drastic offset in the pH reading. Teflon is substituted for the

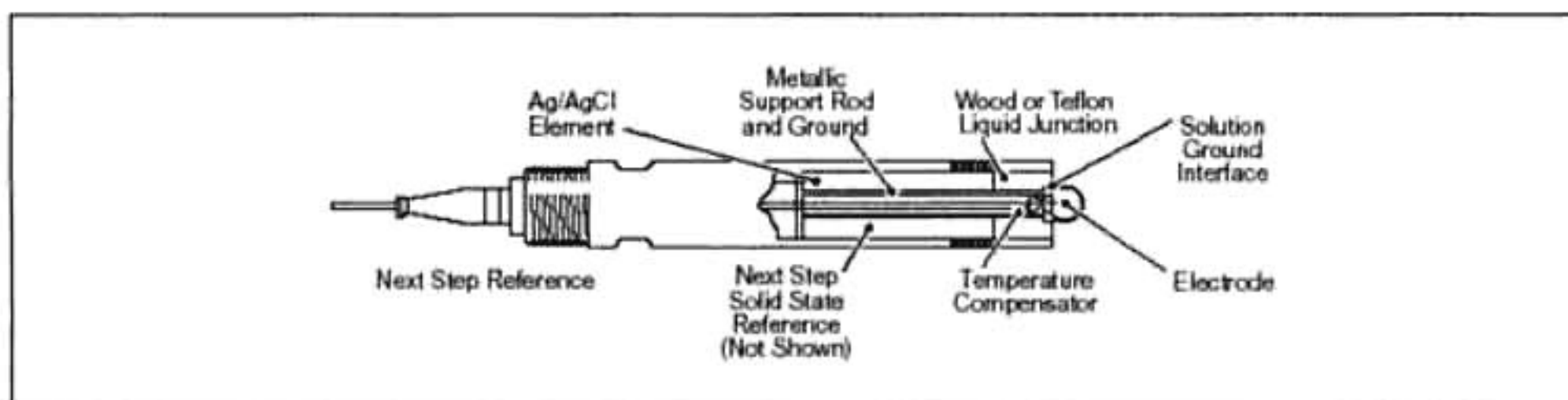




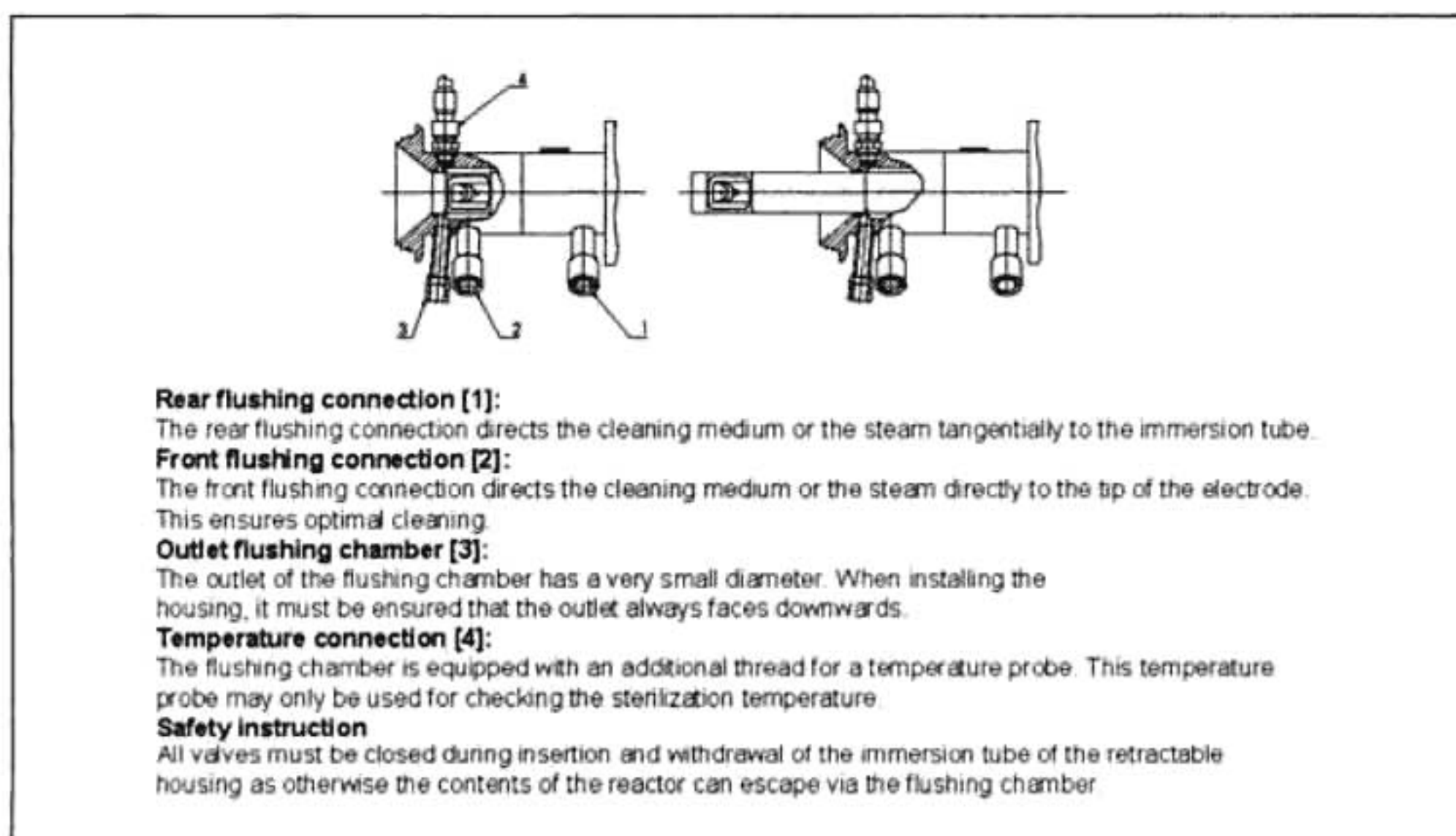
**Figure 4-3a. Solid TUpH Reference Electrode with Micron-Size Helical Pathways (Courtesy of Rosemount)**

dowel in contact with the process for applications requiring a sanitary surface or with chemicals that attack wood, such as hydrogen peroxide and hot, concentrated sodium hydroxide. Teflon is more difficult to keep saturated, and slows down the time to equilibrium. This slowness is an advantage for continuous pH control where it is desirable to ignore fluctuations in ionic strength from the steady state. However, it is difficult to get the electrode to match buffers within 0.1 of a pH for a two-point calibration. Since installation effects of more than 0.2 pH are normal, tight agreement with buffer solutions is not indicative of the electrode's installed performance. For high ionic strength process streams, high ionic buffers are recommended to precondition the electrode. A process calibration is essential for solid state electrodes. For some batch applications, the reference does not have time to reach equilibrium, and pH errors of 0.5 pH and larger occur. In batch operations, it is important to use a wooden dowel if possible for the reference junction to make it faster.

Ingold patented a Xerolyte™ stiff polymer reference electrode. It uses an aperture diaphragm to provide direct contact between the process and reference electrolyte. It has performance advantages in streams with high salt concentrations, emulsions, suspensions, proteins, sulfides, hot alkalies, and pressure fluctuations, particularly when combined with the flushing chamber shown in Figure 4-3c. However, the solid polymer is not suitable for stream sterilization, large temperature changes, or extremely acidic media (below 2 pH).



**Figure 4-3b. Solid Reference that Is Nearly Impervious to Contamination (Courtesy of TBI-Bailey)**



**Figure 4-3c. Polymer Reference Electrode with Flushing Chamber (Courtesy of Mettler-Toledo)**

Great Lakes Instruments patented a differential reference electrode shown in Figure 4-3d, using a second glass measurement electrode (behind a double junction) in a buffer solution for the reference electrode. The glass bulb isolates the silver-silver chloride element of the reference from sulfides and nitrates in the process. The buffer solution is chosen to be compatible with process fluids to ensure a constant buffer pH and constant reference potential. A ground rod eliminates errors and noise from ground potentials. The smaller positive ions in the buffer solution tend to move through the reference junction, out into organic and pure water streams. This creates an offset in the pH reading. The differential electrode has an excellent performance record in streams with inorganic acids and bases and sulfides such as wastewater.

Amagruß patented the Refex<sup>TM</sup> non-porous reference electrode shown in Figure 4-3e that uses an ionic electrochemical conductive salt loaded into a polymeric matrix. There is no contact between the process liquid and the internal KCl electrolyte or Ag/AgCl half cell. Since there is no porous



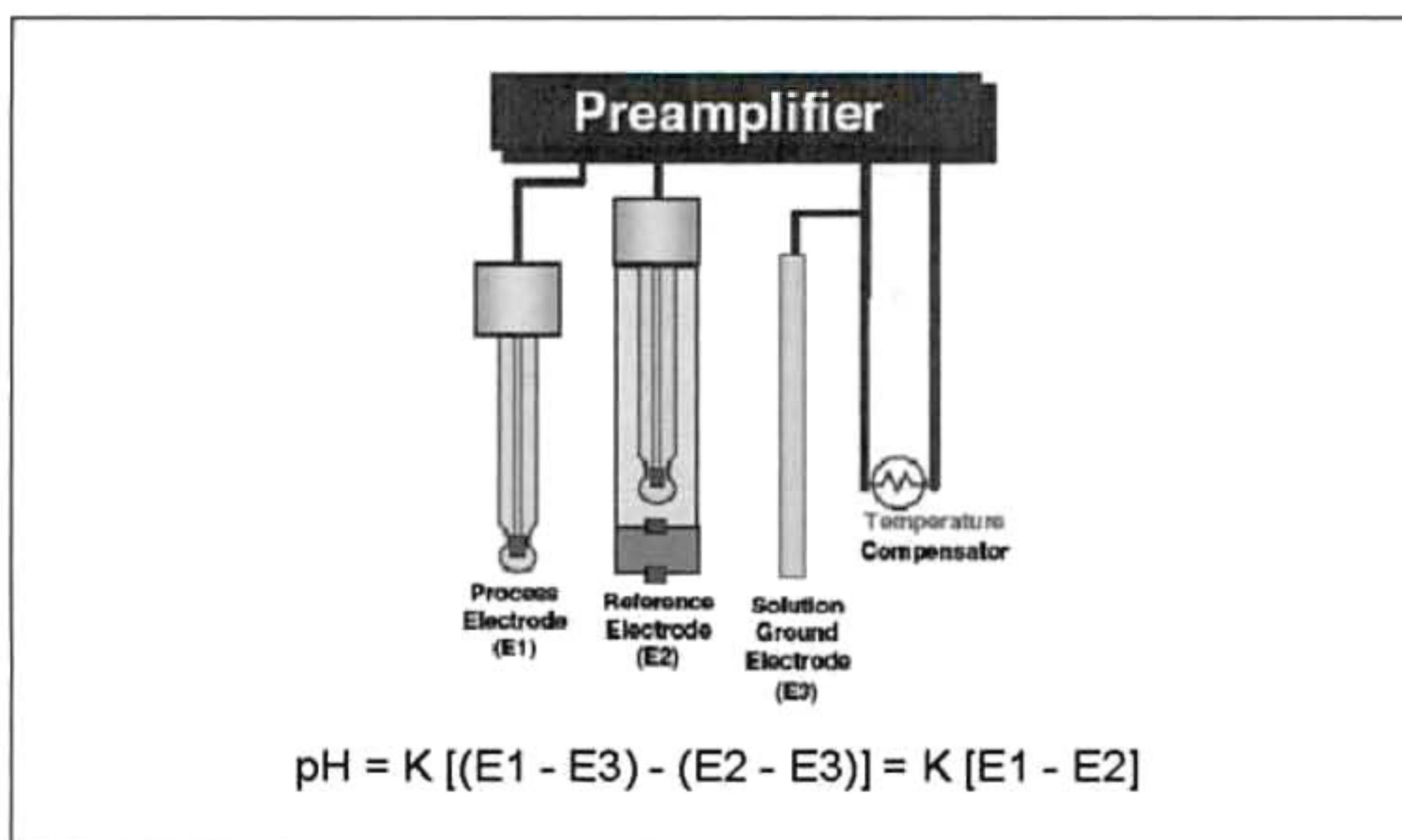


Figure 4-3d. Differential Electrode Completely Isolates Internal Element (Courtesy of Great Lakes Instruments)

junction, there is no migration of electrolyte ions or process ions into the junction. Consequently, there is no threat of contamination and no diffusion potential or time required to reach equilibrium. Thus, it is a candidate for batch, high and low ionic strength, and non-aqueous processes and streams with sulfides or cyanides that might cause precipitation. Also, coatings have no affect on accuracy other than via an increase in circuit resistance since there is no penetration or clogging of a junction. However, a coating of the glass bulb will dramatically slow down the response as it will for any measurement electrode. The reproducibility for different process conditions and replacement electrodes needs further documentation since a different attempt at this design concept suffered from a variability of matrix loading during manufacturing.

#### 4-4. Application-Based Selection

For applications that demand an exceptional installed reproducibility of better than 0.05 pH, the best technical choice is a spherical glass measurement electrode and a flowing junction reference electrode. The glass must be selected to match the pH and temperature range of the process. The reference electrode aperture area and reservoir pressure must be chosen to maintain a small constant flow of electrolyte into the process. However, this choice of electrode has special installation and maintenance requirements that make them an extremely unpopular choice compared to throwaway solid state combination electrodes. Spherical bulbs are more



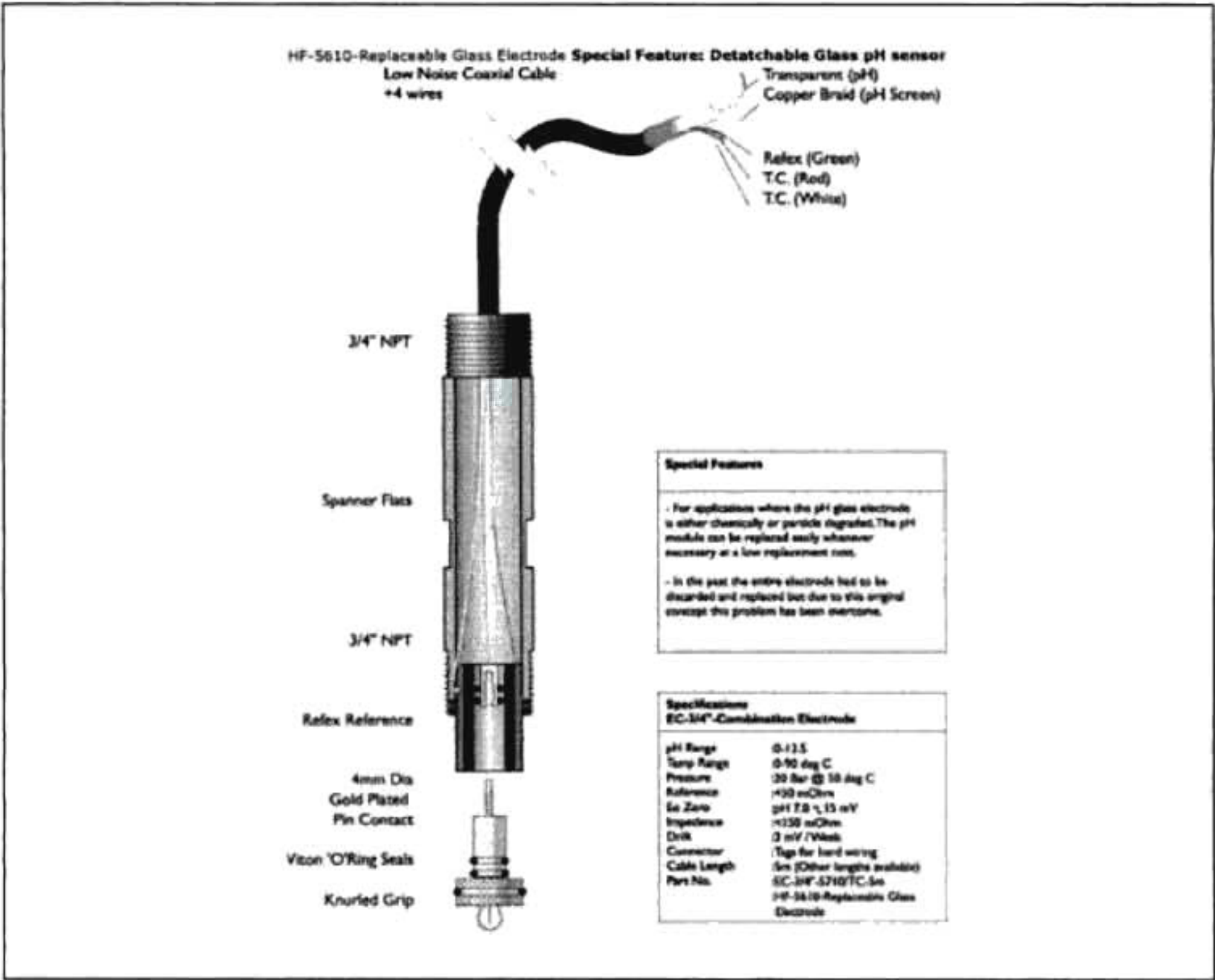



Figure 4-3e. Non-porous Reference Junction Eliminates the Migration of Ions (Courtesy of Refex™ Sensors Ltd)

prone to breakage and must be carefully handled and installed with a properly designed protective shroud per Figure 4-2g. The separate reference electrode is also generally made of glass and requires a separate reservoir regulated to a constant differential pressure above the process pressure.



A glass measurement electrode with a spherical bulb and a reference electrode with a flowing junction offer the best reproducibility important for product quality but are generally unpopular choices with maintenance.

A technician may not understand active gel layers and diffusion junction potentials but will recognize broken glass bulbs and bodies, empty electrolyte reservoirs, additional electrodes, and a mess of tubing and accessories. If the accuracy is not justified and properly explained to the people stuck with dealing with the installation on a day to day basis, the electrodes will soon end up in the junk pile along with your reputation. It is critical to remember that any electrode forced on maintenance and



operations will not only fail but fail miserably no matter how good the selection matches up with the application. We have seen electrodes that were technically not the best choice but they succeeded because the technicians and operators believed in them. The best bet is to get these people involved in the selection process and if possible make them think they made the choice.



**The best choice might not be the best technical match to the application but the electrode with the best support by maintenance and operations.**

Fortunately, few applications actually require a reproducibility of better than 0.05 pH. It is important to realize that most chemists and process engineers set accuracy requirements that are unrealistic both in terms of practical value and attainment. Since they are generally thinking in terms of what they can do in a laboratory environment and often lack first-hand experience with errors in field installations and documentation of the actual effects on the process operation, the requirements are often unrealistic. The result is over calibration and excessive maintenance costs. One solution is to make this chapter required reading before a general discussion of the real accuracy requirements.



**The accuracy requirement often stated by process engineers and chemists is unrealistic and should be corrected to a more reasonable expectation.**

In any unproven process application, it is critical to test a selected electrode at actual process conditions before committing to a permanent installation. Of course, this is best done by a field trial where the electrode is inserted into the process at the proposed point of pH control and compared to lab samples for at least a month. Manufacturers are willing to provide the electrodes and assistance on the basis that you order electrodes and spares if the installation is successful. If there is great uncertainty as to whether an electrode will work at all in the harsh conditions of the process, a preliminary test in the lab at the operating temperatures and velocities is warranted unless the chemicals are too hazardous or difficult to handle or maintain at process conditions. It is not advisable to ship chemicals to the electrode manufacturer for testing because of safety and liability concerns. For the more common chemicals, the manufacturer may be able to develop its own samples or test data for a given range of compositions and operating conditions.





**In any unproven application, it is critical to test an electrode at actual process conditions before committing to a permanent installation.**

For *batch* processes, there is usually insufficient time for a solid-state reference electrode with a porous junction to reach ionic equilibrium. However, if the electrolyte's ions are immobilized and junction has no pores, then a solid-state reference is a candidate since there is no diffusion potential to be established. However, the reproducibility required of pH measurements in batch processes is usually higher than in continuous processes and the flowing reference junction and spherical glass bulb electrode are generally the best choice. The flowing reference reduces the possibility of penetration and entrapment of microorganisms or products in the junction and possible contamination of batches. For less demanding batch applications in the food and water treatment industry, a non-porous or differential reference electrode and ISFET or flat glass measurement electrode may be an option. For sanitary applications, the electrode must be able to withstand repeated sterilizations, and the installation assembly and connection must not have any crevices.



**Batch applications require greater measurement reproducibility that necessitates the reference's diffusion potential be small and rapidly established.**

For *continuous* processes, the slowness of a solid-state reference electrode can actually be an advantage by ignoring short-term changes in process ion concentration and type. However, in high ionic strength streams, it may take hours for the reference to reach ionic equilibrium after installation. In these applications, it is beneficial to calibrate and soak the electrodes in buffers that are loaded with salt ions of a concentration and type similar to what exists in the process stream and to minimize the number of times the electrodes are removed for cleaning or calibration. In general, for continuous processes the electrode selection depends more on what type of electrode will last the longest and require the least service. For chemical processes, the operating conditions can be particularly harsh.



**Continuous chemical processes have a greater need to increase life expectancy and decrease maintenance cost despite high temperatures and pressures, and high concentrations of solids, ions, and hazardous materials.**



For *high temperature* process streams, the glass type and reference internals must be rated for the time duration of the highest temperature, acid, and base concentrations. For example, glass electrodes in hot acidic and basic media should use E and L type glass in Figure 4-2a, respectively. The alkalinity error is larger and the chemical attack is dramatically greater at high temperatures. The life expectancy of the electrode falls off exponentially with temperature, acidity, and alkalinity. Figure 4-4a shows a rough approximation of the operating conditions where the use of glass requires caution or is not advisable. The table assumes the correct type of glass is selected for the pH and temperature range. Notice that the ratings deteriorate more quickly for high pH. For streams above 12 pH and 45°C, the life expectancy of glasses is unacceptable for continuous exposure. For streams below 130°C, the upper limit of the glass electrode, an automatically retractable assembly can reduce the process exposure. For temperatures of less than 120°C within an operating range of 1 to 6 pH, the Glasteel™ electrode is an option to increase life expectancy. For higher temperature streams, the choices narrow down to a sample cooler or a zirconia electrode.



**Life expectancy exponentially declines with temperature and the combination of a high temperature and high caustic concentration is disastrous.**

The most viable alternative to prolong the life expectancy of electrodes in a hot stream is an automatic retractable assembly. As with any electrode assembly, the materials of construction must be checked for the chemicals and temperature. Corrosion increases at higher temperatures so more attention must be made to all wetted parts. Solutions can be switched to condition, diagnose, and calibrate the sensor, and the insertion versus the retraction time can be optimized. To avoid thermal shock, the probe should be kept in a relatively hot but neutral solution for condition. For the most severe service ratings, the electrode would end up being retracted for 2 minutes or more since the response time (time to 98% of final value) is at least 0.2 minutes for even a clean electrode. This sample and hold methodology adds an average dead time of about half the retraction time and can only attenuate the peak error of upsets whose time constant is larger than the dead time. Thus, a large back mixed volume at or upstream of the control point is essential.



**For moderately high process temperatures and large back mixed volumes, use automatic retractable assemblies to reduce process exposure.**



If a heat exchanger is installed to cool the sample, the process temperature must be accurately measured at the electrode and the pH measurement corrected for the effect of the cooled temperature on the dissociation constants. Lab samples must be run at the same cooled temperature. Also, the additional dead time in the loop from the transportation delay through sample lines and the sample cooler must be minimized.



*For extremely high process temperature and large back mixed volumes, use tightly temperature controlled coolers and compensated electrodes.*

The additional dead time from the cycle time of an automatically retractable sensor or the transportation delay of sample cooler system make the pH loop a candidate for model predictive control (MPC) as discussed in the advanced control section of Chapter 8. The execution of the MPC should be synchronized with the cycle of the retractable assembly to minimize the variability of the dead time from the cycle time.

Some manufacturers, such as AMEL Instruments, have started to commercialize Zirconia pH electrodes for temperatures higher than 160°C. These electrodes could potentially handle much faster disturbances, but the long-term drift in actual process applications needs further investigation. Even though the speed of response may degrade with time, the large transportation delay associated with sample systems has been eliminated.

For *solids*, the goal is to keep the glass surface and reference junction clean and in good condition. The best inherent method to prevent the start of many coatings is to increase the fluid velocity to 7 feet per second. However, high velocities are not effective at removing existing coatings. Thus, the electrodes must never be exposed to low velocities. The velocities at the electrode tips of submersion assemblies and flow through cell holders rarely exceed 1 fps. High velocities are usually achieved by the use of retractable or insertion assemblies in recirculation lines. Abrasion increases with velocity along with the risk of damage from clumps of material and foreign substances. Therefore, it is important that electrodes be installed downstream of pumps that have suction strainers.



*For non-abrasive solids, installation in a recirculation line with a velocity of 5 to 9 fps downstream of a strainer and pump may prevent coatings.*

Velocity affects the pH reading by changing the rate of dispersion of the ions in the porous reference junction and thus the liquid-liquid junction or diffusion potential. This can translate to drift or short term fluctuations depending upon the rate of change of the velocity. The velocity should be controlled at an optimum value, particularly for pure water and non-



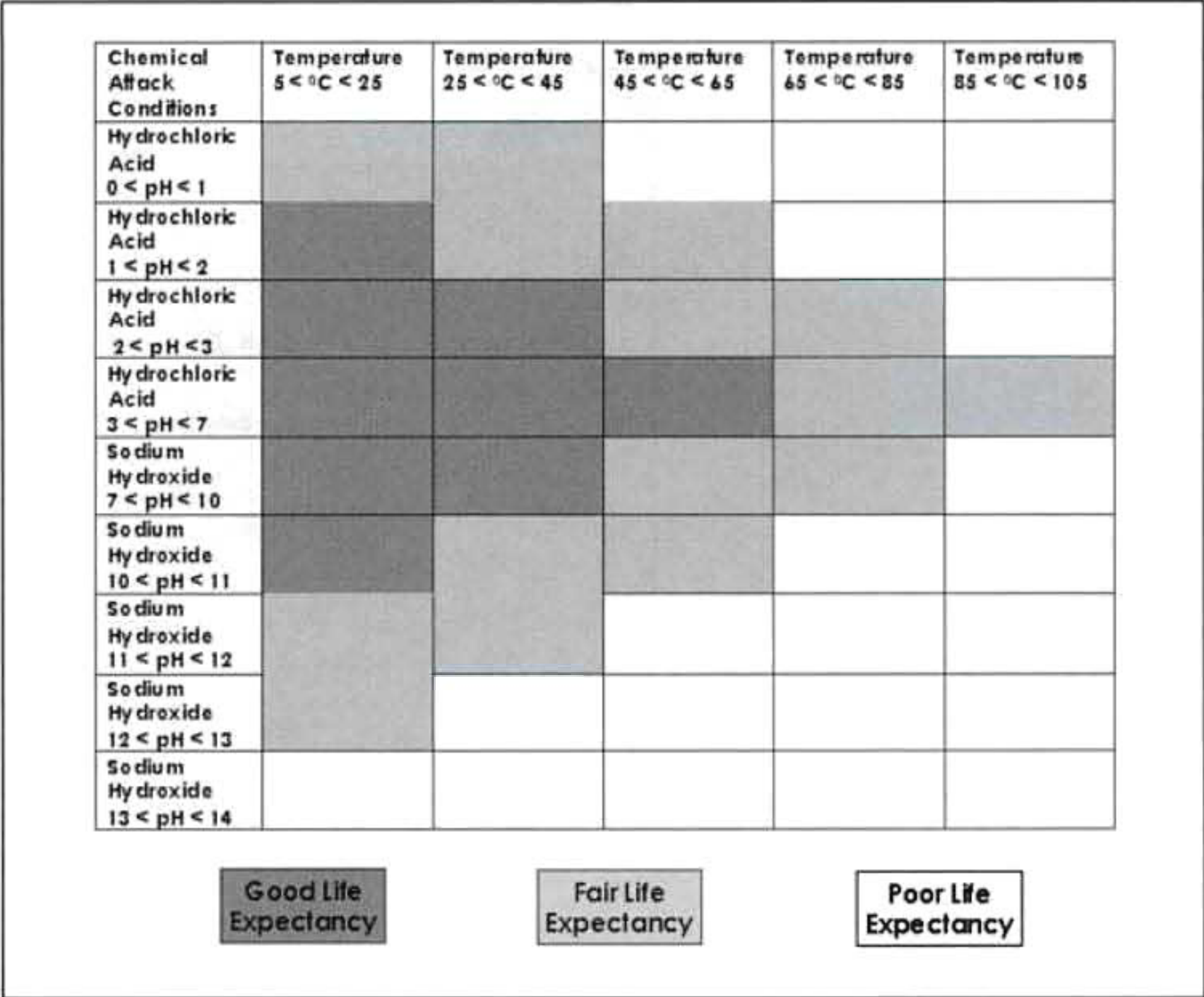




Figure 4-4a. Temperature Ratings of Glass Electrodes in Terms of Life Expectancies

aqueous streams. Velocities higher than 10 fps create more noise and reduce the life of the glass for all applications.

 *The velocity at the electrode tip should be controlled at an optimum value to reduce maintenance, drift, and noise.*

Flat surface glass electrodes such as that shown in Figure 4-4b can provide an effective sweeping action at a much lower velocity and eliminate the separation of the flow stream and stagnation that occurs on the back side of a glass bulb. Thus for abrasive, sticky, and viscous streams, flat surface glass can decrease the fouling and stagnation and enable a faster and more representative measurement of changes in the 2 to 12 pH range. The 1 fps velocity in a flow through holder may be sufficient to keep the glass clean.

 *For abrasive solids and viscous fluids, a flat glass electrode can minimize coatings, stagnant areas, and glass breakage.*

If a spherical glass bulb measurement electrode must be used, jet washers can be used to provide in-service cleaning. High velocity nozzles pointed





**Figure 4-4b. Ruggedized Flat Glass Dolphin™ Electrode with a Fine Porosity Reference**  
(Courtesy of Foxboro)

at the bulb are an option for submersion and flow through assemblies. The pH controller should be automatically switched to manual during the jet washing because the signal will be erratic. If the cleaning solution contaminates the process, automated retractable assemblies can be used to withdraw the electrodes from the process into a chamber where it is flushed, cleaned, calibrated, and conditioned by switching in appropriate streams. The controller should be automatically switched to manual when the electrodes are retracted. Note that it is not sufficient to just freeze the last pH measurement because it is never exactly equal to the set point, and reset action in the pH controller will continue to drive the output to eliminate the offset. The last thing you want in terms of maintenance cost, electrode life, and safety is for technicians to be manually cleaning electrodes. Any rubbing and handling of electrodes reduces their life expectancy and reproducibility.



*When the fluid velocity is insufficient to sweep electrodes clean, use an integral jet washer or a cleaning cycle in a retractable assembly.*

For non-flowing reference electrodes, it is important that the reference junction have no pores and have an active surface area as large as possible. Once particles get stuck in the pores, they are extremely difficult to remove. The plugging of the reference junction isolates the electrolyte from the process and increases the electrical resistance and time to equilibrium. A larger junction surface area increases the chance that part of the junction is still free but increases the contamination rate from process ions moving into the reference. gel filled reference combination electrodes slow down the contamination rate but not as much as a solid state references, which enables the use a large junction area that is either



the sleeve or annular ring around the glass measurement electrode. Cone and sleeve annular flowing junctions not only prevent plugging and contamination but also offer a faster and more reproducible reference potential.



*To prevent particles from plugging a non-flowing reference junction, use a non porous or aperture junction solid-state reference electrode.*

For *high pH* streams, the concerns are alkalinity error and chemical attack of the glass. While alkalinity error is often plotted versus pH as in Figure 4-2c and 4-4c, it does not have to be associated with high pH because it could be caused by the presence of high concentration of a salt such as sodium chloride, instead of sodium hydroxide (caustic).

*Alkalinity or sodium ion error* is caused by alkali ions such as sodium ions penetrating the measurement electrode silicon oxygen network and displacing the hydrogen ions in the gel layer, which causes a decrease in the hydrogen ion activity of the gel layer relative to the process and a decrease in the measured pH. The high pH end of the millivolt versus pH line bends upward as shown in Figure 4-4d, which results in an indicated pH that is lower than the actual pH. The error is greatest for glasses with alkali ions of equal or larger radius than that of the alkali ions in solution. Glasses with small alkali ions, such as Lithium, are called "tight matrix." Alkalinity error is called sodium ion error because sodium ions are more prevalent and more of a problem due to the popularity of sodium hydroxide as a reagent and the smaller radius of the sodium ion and hence, the greater capability to penetrate the matrix compared to the next most common alkali ion, the potassium ion. The alkalinity error of Corning 015 glass for process streams with lithium and potassium ions is about twice and one fifth, respectively of that for sodium ions due to their relative size. The alkalinity error also increases with temperature. For example, the alkalinity error of Corning 015 glass starts at 9.5 pH at 30°C, 8.0 pH at 50°C, and between 5 and 6 pH at 60°C. The heat of neutralization from sodium hydroxide can cause a significant unsuspected alkalinity error for a 7 pH set point. Glass formulations have been made that reduce the alkalinity error but with some sacrifice as to non-linearity over the 0 to 14 pH scale. Figure 4-4c shows that the correction pH increases exponentially with pH above some threshold level. Note that the solution pH is equal to the measured pH plus the correction pH and that the pH error is equal to the negative of the correction pH.

For *low pH* streams, the concern is the acid error and dehydration of the glass surface from an acidic environment. While high temperatures do not greatly increase the acid error, extremely hot acidic streams, dramatically decreases the glass's life expectancy.



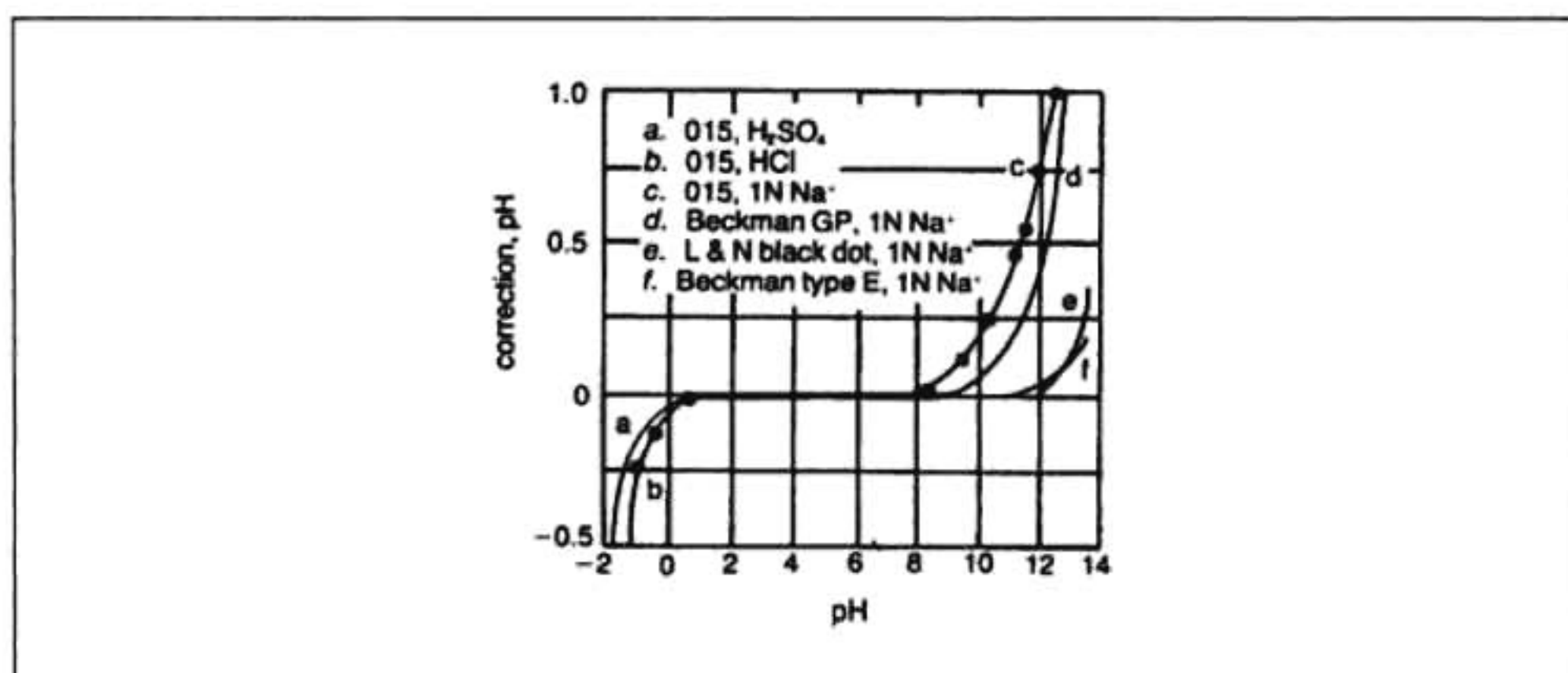


Figure 4-4c. Alkalinity and Acid Error as Function of pH for Various Glasses

The cause of the *acid* error at the low end of the pH scale is not as well understood. Tests show that the gel layer absorbs acid molecules and increases its hydrogen activity relative to the process, which increases the pH reading [Ref. 4.13]. The onset of the acid error is marked by a reduction in thickness of the outer hydrated gel layer of the measurement electrode. The low pH end of the millivolt versus pH line bends downward as shown in Figure 4-4d, which results in an indicated pH that is higher than the actual pH. The sign of the pH error is opposite of that for the alkalinity error. The error is independent of temperature but increases with time. Thus, significant upscale pH measurement drift at the low end of the pH scale is symptomatic of the acid error. The initial acid error of Corning 015 glass electrodes is 0.2, 1.7, and 8.9 pH for 3, 12, and 18 molar sulfuric acid, respectively. Since acid error does not start above 1 pH, acid error is not a problem for feedback loops because their set point is at a higher pH. However, some pH feedforward loops of strong acid influent have developed significant errors and failed. Figure 4-4c shows that the initial pH correction magnitude increases exponentially as the pH decreases below 0.5 pH.



*For high and low pH streams, use special glass formulations and retractable electrodes or sample coolers to prolong the glass's life expectancy.*

*Hydrofluoric acid* will etch glass below 3 pH. Since most pH controller set points are higher, the solution is to ensure the pH control is tight enough to reduce the number and duration of pH excursions below 3 pH. When this is not possible, antimony electrodes are used. Iridium Oxide and Zirconia probes are a future possibility.

Antimony measurement electrodes are a last resort when the chemical attack of caustic, etching of hydrofluoric acid, wear and cracking from abrasive particles, or the degradation from high temperatures of glass are



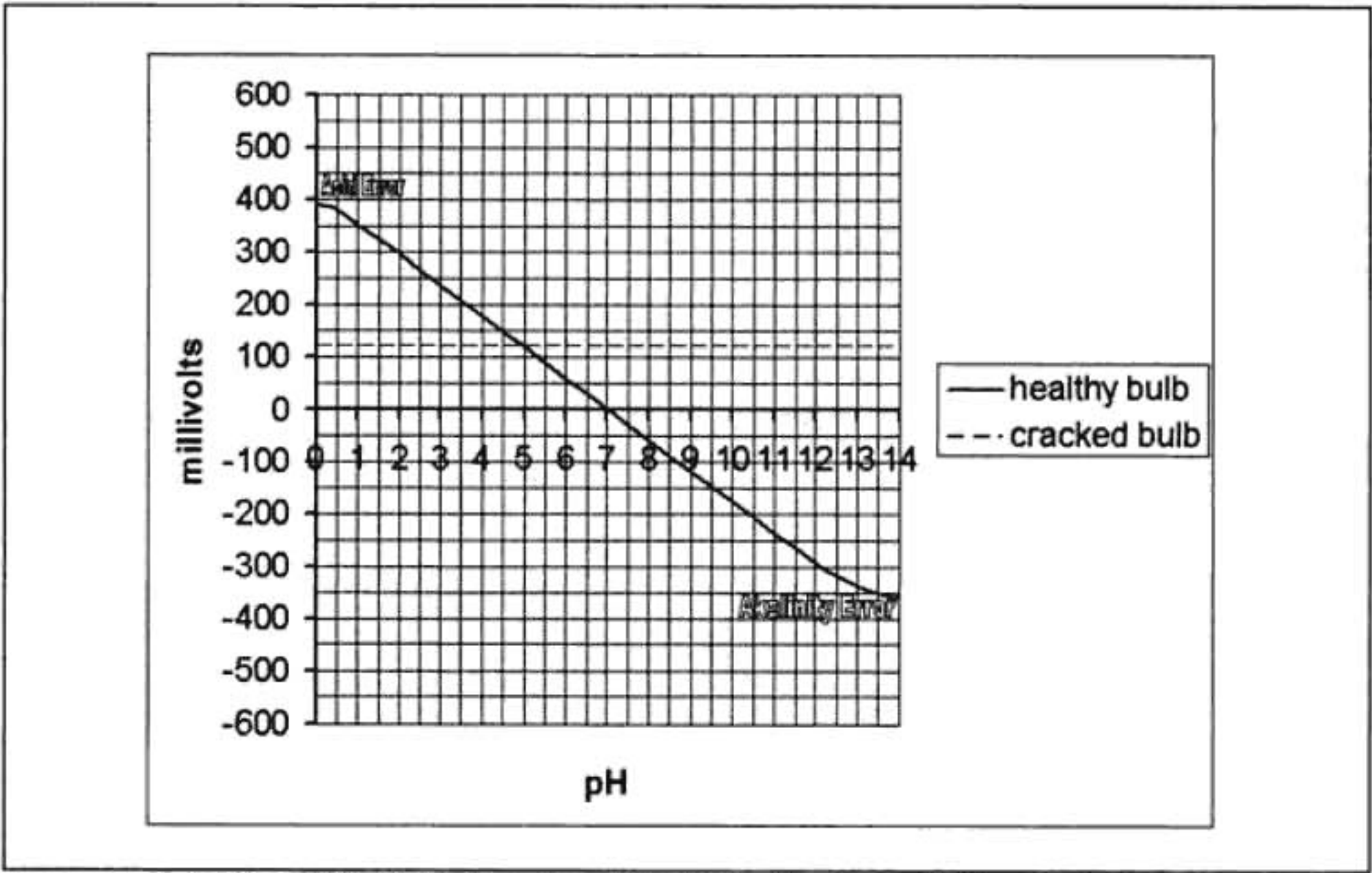


Figure 4-4d. Acid and Alkalinity Error Bend the Millivolt versus pH Line

excessive. However, antimony like all metal electrodes develops an oxide coating that must be periodically scrubbed off and acts as an oxidation reduction potential (ORP) probe.



*For hydrofluoric acid, the best bet is to use a rugged glass and prevent excursions below 3 pH and only use a metal-oxide electrode as a last resort.*

For *non-aqueous* solutions where there is a different solvent than water, the issues are bulb dehydration, electrical resistance, electrolyte precipitation, and the relative nature and expanded range of the pH scale.

To minimize the effect of bulb dehydration and the increase in solution electrical resistance, it is important to use a large spherical area bulb with a low resistance glass. Since this type of bulb is more susceptible to breakage it is important to shield it from direct impingement and reduce the fluid velocity as much as possible without increasing the propensity for coatings. The hydrated gel layer will periodically need to be replenished, which is best accomplished by an automated retractable sensor. The electrodes should be cleaned with solvent that will dissolve process solutes, rinsed with a volatile solvent (e.g., acetone, to remove the cleaning solution), and finally soaked in plant water to replenish the gel layer. Any calibration check should be in buffers with the same solvent as the process stream. As with other low conductivity fluids, there is a heightened sensitivity to fluid velocity and streaming potentials from static charges.



The normal potassium chloride (KCl) saturated in water electrolyte should not be used because KCl will precipitate in a non-aqueous solvent, the water forms a separate phase, and the ions migrating into the junction will have unequal mobility setting up a large diffusion potential. It is easiest to change the electrolyte in the outer chamber of an internal salt bridge in a double junction reference electrode. An external reservoir and salt bridge can be used to minimize the frequency of refilling the electrolyte and provide a greater level of protection. Some of the more common choices for electrolyte solutions for a non-aqueous process are Lithium Chloride (LiCl) in acetic acid, ethanol, or methanol, and Potassium Iodide (KI) in acetic acid, acetone, or methanol. Candidate solutions should be tested by soaking the electrodes overnight in the process and measuring the drift.



*For non-aqueous solutions, large low resistance spherical bulbs and non-aqueous electrolyte, cleaning, soaking and buffer solutions are needed.*

The pH of a non-aqueous solution can be below 0 pH for an acidic solvent, such as acetic acid, and be above 14 pH for a basic solvent, such as an amine. The pH measurements can only be compared to measurements in the same solvent because the dissociation constants, the solvent's dielectric constant, and ionic mobility will all be different. The neutral point is not necessarily 7 pH. For example, the neutral point of methanol is 8.42 pH and ethanol is 9.55 pH at 25°C on the water-based scale [Ref. 4.14]. The buffer solvent should be as similar as possible to the process solvent. If a batch process moves from an aqueous to a non-aqueous composition, the readings cannot be compared between phases but an automatic retractable assembly can enable cleaning, buffer, and soaking solutions that match up sensor calibration and conditioning with the batch phase. If the water content drops below 5%, the solution can be considered to be non-aqueous [Ref. 4.2]

*High ionic strength* streams increase the reference junction potential and decrease the activity of the hydrogen ion. Unless the ions can penetrate the glass, the biggest adverse effect is the drifting potential of the reference. It may take hours to days for a nonflowing porous reference junction to reach ionic equilibrium. In general, gel fill is slower than liquid fill reference, double junction is slower than single junction references, and a solid state is the slowest of all the references. To improve the accuracy of the electrodes and hasten the approach to equilibrium, high ionic strength buffer solutions should be used for calibration and soaking (preconditioning). To create these buffer solutions, salts similar to what are in the process that are compatible with the buffer are added so that the ionic strength defined per Chapter 2 of the buffer is close to that of the process solution.





*For high ionic strength solutions, use a fast reference electrode that is calibrated and preconditioned in high ionic strength buffer solutions.*

Low ionic strength streams, such as pure water, the electrical resistance of the solution is high making the measurement more susceptible to electrical noise and streaming potentials. Low resistance glass and large spherical bulbs and an upstream liquid reference electrode should be used. The electrode assembly should be shielded from electrical fields and isolated from ground potentials [Ref. 4.15]. The solution temperature should be measured. The sample flow rate must be regulated to keep the velocity low and constant. Figure 4-4e shows an integrated assembly with these features for pure water applications, such as boiler feed water, demineralized water, and deionized water.

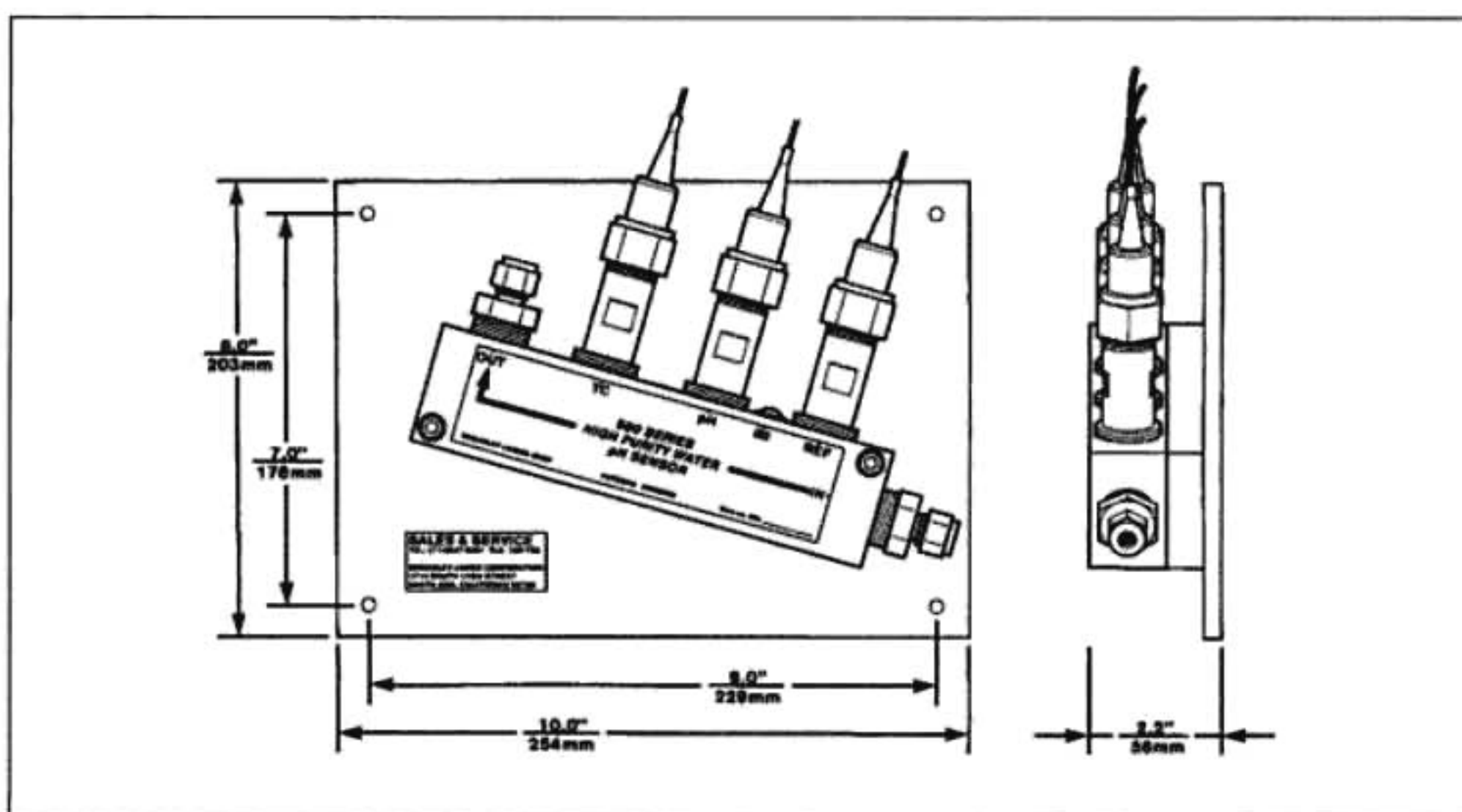


Figure 4-4e. Pure Water Assembly to Reduce Noise from Streaming Potentials, Ground Potentials, and Electrical Interference. (Courtesy of Broadley-James)



*For low ionic strength solutions, use a large spherical low resistance bulb and minimize the noise from potentials and electrical interference.*

For cyanides, bromides, iodides, sulfides, or nitrates, the concern is the reactive precipitation of the silver and potassium chloride in the electrolyte observable as a blackening of the junction. The solution is to use an electrolyte in an internal or external salt bridge that is compatible with the process, a differential electrode, or a solid-state reference electrode with an immobilized electrolyte or a non-porous junction.



*For sulfides and nitrates, use a special electrolyte in a salt bridge, a differential electrode, or a non-porous reference.*

For *fluctuating and high pressures*, the principle concern is the separation and contamination of the reference electrode. Gel filled electrodes can develop voids. Liquid filled electrodes will suck in process fluids when the pressure in the process is greater than in the reference. solid-state or pressurized reference electrodes with an internal or external salt bridge should be used. Ideally, the differential pressure between the process and the salt bridge should be constant to maintain a constant flow of electrolyte.



*For fluctuating and high pressures, use a solid-state or pressurized reference electrode with an internal or external salt bridge.*

For *concentrated surfactant solutions*, the reference junction potential rapidly shifts and the surfactants tend to “salt out” in the reference junction when they contact the concentrated electrolyte solutions. Since the surfactants are conductive, neither of these effects correlate with reference junction impedance. The only way to detect these problems is to remove the sensor from the surfactant, rinse with deionized (DI) water and then place it in a buffer solution. Depending on the concentration of the surfactant and the length of process exposure, you may observe an offset in the range of 0.2–0.8 pH [Ref. 4.4].

## 4-5. Smart Transmitters

Smart pH transmitters not only do the standard CPU, continuity, and I/O checking but also measure the circuit resistances between the measurement and reference electrode inputs and the solution ground. The diagnostics must include changes in glass resistance with temperature and for low conductivity process streams should also include the change in fluid resistance with temperature. A large decrease and increase in the resistance of the glass indicates a broken or dehydrated electrode, respectively. A large increase in the resistance of the reference electrode indicates that the reference junction is coated or plugged with a non-conducting material.

The best way to detect a coated measurement electrode is not from electrical resistance but from the speed of response to pH changes. The additional electrical resistance from the process coating is typically small compared to the resistance of the glass. A thin almost imperceptible film can dramatically slow down the migration of hydronium ions and increase the time constant of the electrode from a few seconds to several



minutes. For loops in automatic, a slow measurement electrode shows up as either an increase in the loop's oscillation period or settling time depending on the controller tuning and coating thickness. If there is more than one pH electrode, the coated electrode always will lag behind the clean electrode. For a ramping disturbance, the lag time is approximately the additional time constant of the coated electrode. If an automated retractable assembly is used, the time constant in a buffer solution can be measured. However, the flushing and cleaning cycle may remove the coating. To diagnose the coating that existed while in service and the effectiveness of the cleaning cycle, the time constant of the electrode should be checked before and after flushing and cleaning. As previously mentioned in the section on electrode selection for solids, it is not sufficient to just freeze the reading. The pH controller must be put in manual. There needs to be extensive communication between the control system, performance monitoring system, smart transmitter, cleaning system, and maintenance system. Ideally, a smart transmitter or performance monitoring system signals an impending need to clean or replace a probe. The control system decides if this is a good time based on production and process requirements and the severity of the problem, puts the pH controller in manual, and signals the cleaning system to start its cycle. For batch operations, normally there are certain steps where the pH electrode is not used and for continuous operations there may be time when the unit can run at reduced rates. The cleaning system diagnoses the "before" and "after" time constant and accuracy of the probe and tells the pH control system when it is done and if the electrode is good enough to go back in service. The control system then makes the decision when to put the pH controller back in automatic. All of the diagnostics from operation and cleaning are communicated to the automated maintenance system. A suggested flow of information is shown in Figure 4-5a.

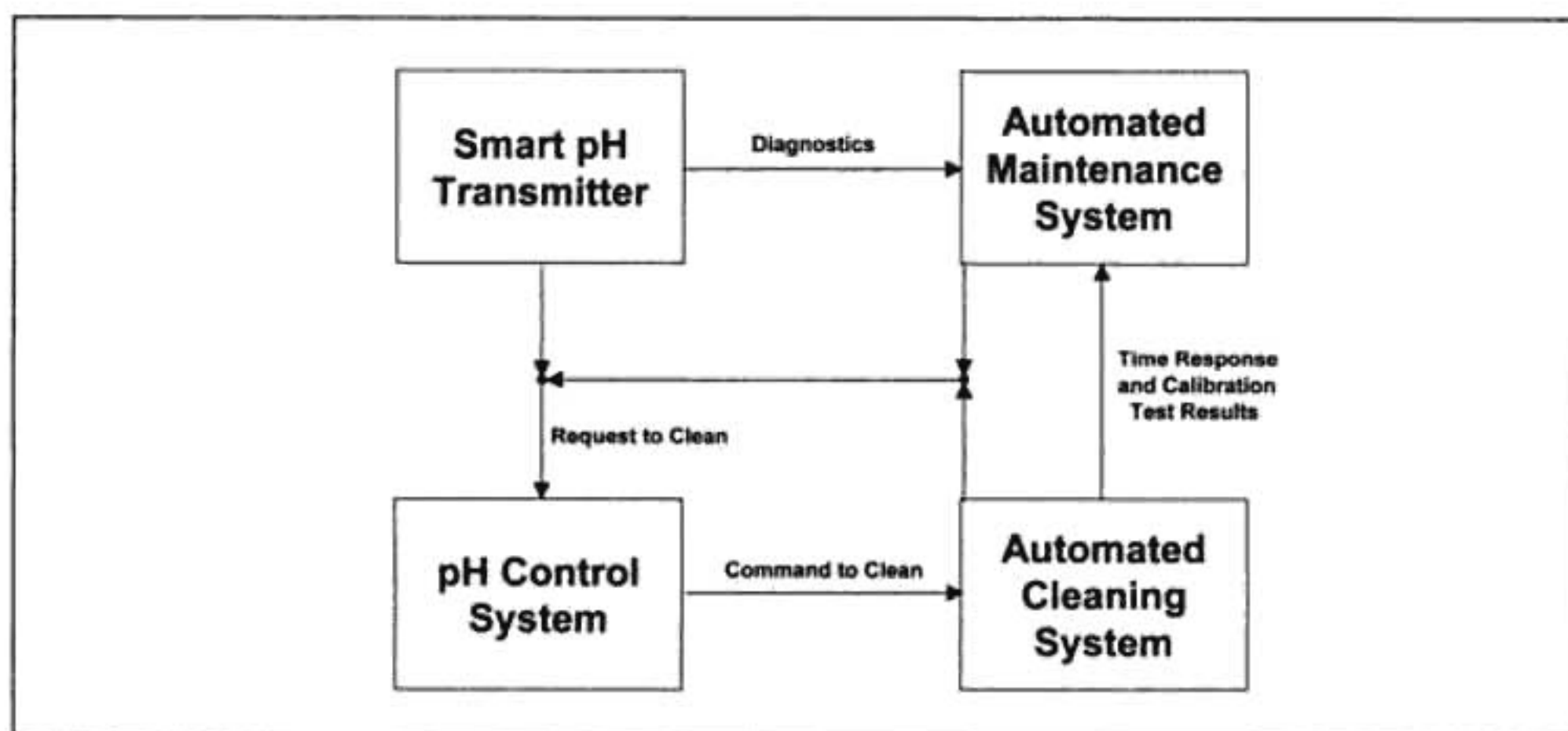


Figure 4-5a. Flow of Information for Automated Maintenance of pH Electrodes





**Performance monitoring, cleaning, control, and automated maintenance systems and smart transmitters must not make unilateral decisions.**



*The control system should schedule automated maintenance based on the severity of the problem and production and process requirements.*

A pH measurement should be a prime candidate for smart transmitters and automated maintenance systems because the life expectancy is shorter and the performance degrades more with process conditions than with any other measurement commonly used in industry.

## 4-6. Failure Protection

It is difficult to predict the failure mode of pH electrodes because they can fail anywhere on or off the pH scale. However, the middle selection of three pH measurements will inherently ride out the first measurement failure of any type. It will also ride out a second measurement failure if it is in the opposite direction of the first. The implementation is straightforward in modern control systems since there is a Fieldbus function block that offers middle signal selection that can be used in the field or in a field-based Distributed Control System. It is important to use the middle measurement and not a median or average measurement. In misguided attempts to do something better, configurations have been developed to reject one signal based on expert system type rules and then average the remaining two measurements; however, these rules cannot possibly cover all the bases and will eventually end up doing more harm than good. Middle signal selection is simple and foolproof. Equipment and piping should have the connections for three probes but a plant should not go to the expense of installing three measurements until the life expectancy has been proven to be acceptable for the process conditions. The user also has to realize that the multiple measurements will never agree and that this is the key to stop chasing short-term transient deviations between electrodes. In the only case where multiple measurements were consistently observed to have the same readings, it was found the electrode tips still had on their protective caps filled with a buffer solution [Ref. 4.16]. If there are Coriolis mass flowmeters and the titration curve can be identified or modeled, an online pH estimator can be developed to replace one of the electrodes.





pH measurements can fail anywhere on or off the pH scale but middle signal selection will inherently ride out a single electrode failure of any type.



*Equipment and piping should have the connections for three probes but a plant should not go to the expense of installing three measurements until the life expectancy has been proven to be acceptable for the process conditions.*



If multiple pH measurement all have the same value for more than a few minutes, the protective caps are probably still on the electrode tips.

The use of three electrodes and middle selection also has numerous other advantages. It will reduce noise and eliminate spikes much more effectively than a transmitter damping adjustment or a process variable filter and without the addition of a lag time to the loop. It will enable predictive maintenance based on the long-term trend of the deviation of an electrode from the middle value. A single transmitter can be taken out of service without switching the controller to manual. A single transmitter can also be calibrated with the controller in automatic unless there is a big spread between the remaining measurements.

The use of two pH electrodes raises more questions than answers because there is no referee other than the lab, which has its own set of problems. However, installations of two electrodes are much more prevalent than 3. There is usually a manual switch that allows operations to select the current favorite but this is based more on “war stories” than logic. High and low signal selectors are used when a downscale or upscale failure, respectively, clearly poses a greater safety hazard. The collaboration of smart transmitters with automated maintenance, cleaning, control, and performance monitoring systems shown in Figure 4-5a will lead to better predictive maintenance and failure protection.

#### 4-7. Dynamic Response of Electrodes, Holders, and Sample Systems

The dynamic response of a clean pH measurement electrode without any problems directly immersed in an aqueous solution can be approximated by the time required to reach 63% of the final response ( $T_{63}$ ). Since the electrode dead time is negligible compared to other dead times in the system,  $T_{63}$  can be viewed as approximately the same as an open loop time



constant ( $\tau_0$ ) whose value varies between 2 and 30 seconds. The use of a time constant is more effective than a response time ( $T_{98}$ ) (time to 98% of the final value) because  $T_{98}$  is difficult in practice to measure in industrial applications due to noise, pH electrodes exhibit an unusually long tail, and the first part of the response is most important for process control. One should get the manufacturer's definition of response time because it may not be  $T_{63}$  or  $T_{98}$  and then convert it to a time constant. The % of final value definition for response time can make a huge difference because  $T_{86}$ ,  $T_{95}$ , and  $T_{98}$  theoretically correspond to 2, 3, and 4 time constants, respectively.



*Get the manufacturer's definition of response time in terms of % of final response and convert it to a time constant for control system analysis.*

The major contributors to an electrode's time constant are a boundary layer of fluid around the electrode bulb that slows down the diffusion and migration of ions to the pH sensitive glass and a double layer effect at the surface of the glass that poses an energy barrier to the proton [Ref. 4.17]. The hydronium ion moves from regions of high to low concentration (diffusion) and moves from regions of high to low positive charge (migration). The boundary layer, which slows down this movement, increases in thickness as the velocity of the stream past the electrode decreases. The time constant for velocities below one foot per second is large enough to deteriorate loop performance. Since the velocity in pumped pipelines is between three and seven feet per second whereas the velocity in sample lines and agitated vessels is usually less than one foot per second, the pipeline injector or insertion type of electrode described in the next section should be considered whenever a location in a pumped pipeline close to the mixing equipment outlet is available. The double layer has the greatest effect in non-aqueous solutions where the measurement electrode time constant may be a hundred or more seconds. It is probably responsible for the time constant for a decrease in pH being about twice as large as the time constant for an increase in pH and for the time constant for buffered solutions being much smaller [Ref. 4.18]. The time it takes for the proton to move to its site in the glass once it jumps the double layer energy barrier has been measured to be about 30 milliseconds by using a jet stream to eliminate the boundary layer and double layer effect [Ref. 4.19]. Table 4-7 summarizes some test results on electrodes for different stream velocities and directions of pH changes for solutions with a high buffer index (flat portion of a titration curve). Not shown is the fact that the time constants get to be several times larger for steep curves. For example, the time constant of solutions with strong acids and strong bases is about 2 and 4 times larger for positive and negative changes, respectively, than what is shown in Table 4-7.



Table 4-7. Electrode Time Constants for a 3 pH Change in a Buffered Solution

Direction	Velocity (fps)	Time Constant (seconds)
Positive	4	0.75
Negative	4	1.5
Positive	2	1.5
Negative	2	3
Positive	1	2
Negative	1	4
Positive	0.5	3
Negative	0.5	12



The low velocity in vessels, flow-through cells, and sample line tees and strong acids and strong bases increase the glass electrode time constant.

A slime coating of 1-mm thickness slows down the migration of hydronium ions to the glass surface enough to increase the measurement electrode’s response time ( $T_{98}$ ) from 10 seconds to 7 minutes [Ref. 4.7]. Chapter 8 will show how a slow electrode response greatly increases the loop’s period and the tendency to oscillate. The amplitude of the measurement oscillations are an attenuated version of the real world pH fluctuations. For thick coatings, a hydronium ion concentration is trapped and the pH reading freezes.

A change in salt concentration will change the electric field and alter the migration of hydrogen ions enough to change the pH until a concentration gradient develops and the diffusion of the hydrogen ions reestablishes the original hydrogen ion activity at the measurement electrode surface. For example, the addition of 0.1 moles per liter of sodium chloride to a 3 pH solution of hydrochloric acid will cause the pH to temporarily drop to 2.9 pH and return to 3 pH about 6 seconds later [Ref. 4.17]. The measured pH goes through a transient even though the true pH has not changed. The control loop must ignore rather than chase such transients, which are essentially noise.

Near the neutral point, the titration curve is steeper and fluctuations from what might be considered to be insignificant concentration fluctuations

are amplified by the high process gain. This can be visualized by plotting a fluctuation on the X axis and translating it to the Y axis of the titration curve. An electrode, transmitter damping, or signal filter time constant will attenuate this noise and make a trend in manual look better but it also slows down the pH controller's ability to see upsets and the results of its own actions. The result is an increase in the loop's period and a tendency to oscillate that increases the loop's settling time. A single back mixed volume and middle selection are the preferred methods to smooth out noise and reduce loop variability in automatic.



**The trend for a large electrode time constant looks less noisy for a loop in manual but shows slow less-damped oscillations for a loop in automatic.**

The time constant and dead time (time delay) from a "flow through cell" or chamber and the dead time from a sample line are frequently larger than the electrode time constant. The chamber is partially back mixed from the turbulence of the incoming flow so that the residence time (volume divided by flow) is split between a time constant and an equivalent dead time. If the turbulence creates an agitation flow equivalent to the sample flow, the split is equal so that the time constant and dead time are both equal to one half the residence time per Equations 4-7a through 4-7d. If these values are small compared to the process time constant as would be the case for a vessel, the distinction of the split is of no consequence and the whole residence time can be considered a dead time since small time constants become equivalent to dead time as shown in Chapter 8.

The dead time can be assumed to be equal to the residence time of the sample line per Equations 4-7b because the small time constant from the velocity profile is usually small compared to the total transportation delay so that it essentially plugs flow (no back mixing). Since the volume of the sample line is equal to the length multiplied by cross-sectional area, the dead time can be decreased by decreasing the length or the diameter of the line or increasing the sample flow. The same relationship holds for the transportation delay from a pumped pipeline. A common mistake is to install a large agitator to reduce equipment dead time and then install the electrodes in a flow through holder or chamber with a long length of intervening sample line or pumped pipeline so that the resulting measurement dead time is greater than the equipment dead time. A heat exchanger in the sample line to lower the sample temperature or in the pipeline to remove the heat of neutralization can add significantly to the



flow path length and hence the transportation delay. Chapter 8 will discuss how the total loop dead time deteriorates loop performance.

The open loop time constant is the residence time of a back mixed volume:

$$\tau_{oc} = \frac{V_m}{Q_s} \quad (4-7a)$$

The time delay (dead time) is the residence time of a plug flow volume:

$$\tau_{dc} = \frac{V_p}{Q_s} \quad (4-7b)$$

For a 50% back mixed equipment volume (flow through cells):

$$V_m = 0.5 * V_e \quad (4-7c)$$

$$V_p = 0.5 * V_e \quad (4-7d)$$

For plug flow (sample lines, pipelines, static mixers, and heat exchangers):

$$V_m = 0 \quad (4-7e)$$

$$V_p = A * L \quad (4-7f)$$

where:

- A = cross-sectional area of a sample line, pipeline, static mixer, or exchanger (sqft)
- $Q_s$  = volumetric flow rate (cuft per minute)
- L = length of a sample line, pipeline, static mixer, or exchanger (ft)
- $\tau_{oc}$  = open loop time constant (minutes)
- $\tau_{dc}$  = time delay or dead time (minutes)
- $V_e$  = equipment volume (cuft)
- $V_m$  = back mixed volume (cuft)
- $V_p$  = plug flow volume (cuft)

## 4-8. Installation Practices

The sensor location should provide the most representative, reliable, and fastest measurement. The electrodes should measure the pH of a perfectly mixed combination of feed or influent streams and reagents with minimum maintenance and time delay and lag.

Electrodes should be installed in homogeneous well mixed zones without bubbles. In some rare cases, electrodes are intentionally inserted in a water





**The sensor location should provide the most representative, reliable, and fastest measurement.**

layer of a vessel used for phase separation, such as a decanter, because there is no liquid mixture and oil or non-aqueous solvents cause maintenance, speed of response, and accuracy problems.

If an electrode is located too close to the point of entry of a reagent into a vessel, there is what is referred to as short circuiting, where the electrodes see the effect of the reagent before it is mixed with the contents of the vessel (Mistake 6 in Figure 1-1e in Chapter 1). If it is located in a stagnant area of a poorly mixed vessel, then it is seeing old and inconsistent mixtures and is more susceptible to coatings (Mistake 10 in Figure 1-1e).

The additional dead time from a delayed and slow measurement increases the loop's period, control error, and sensitivity to nonlinearity. The installation must minimize the number of times the electrodes must be removed for maintenance (e.g., calibration and cleaning). Removal and manual handling increases error and reduces the life of the electrode. The gel layer is altered and the equilibrium achieved by the reference junction is upset.

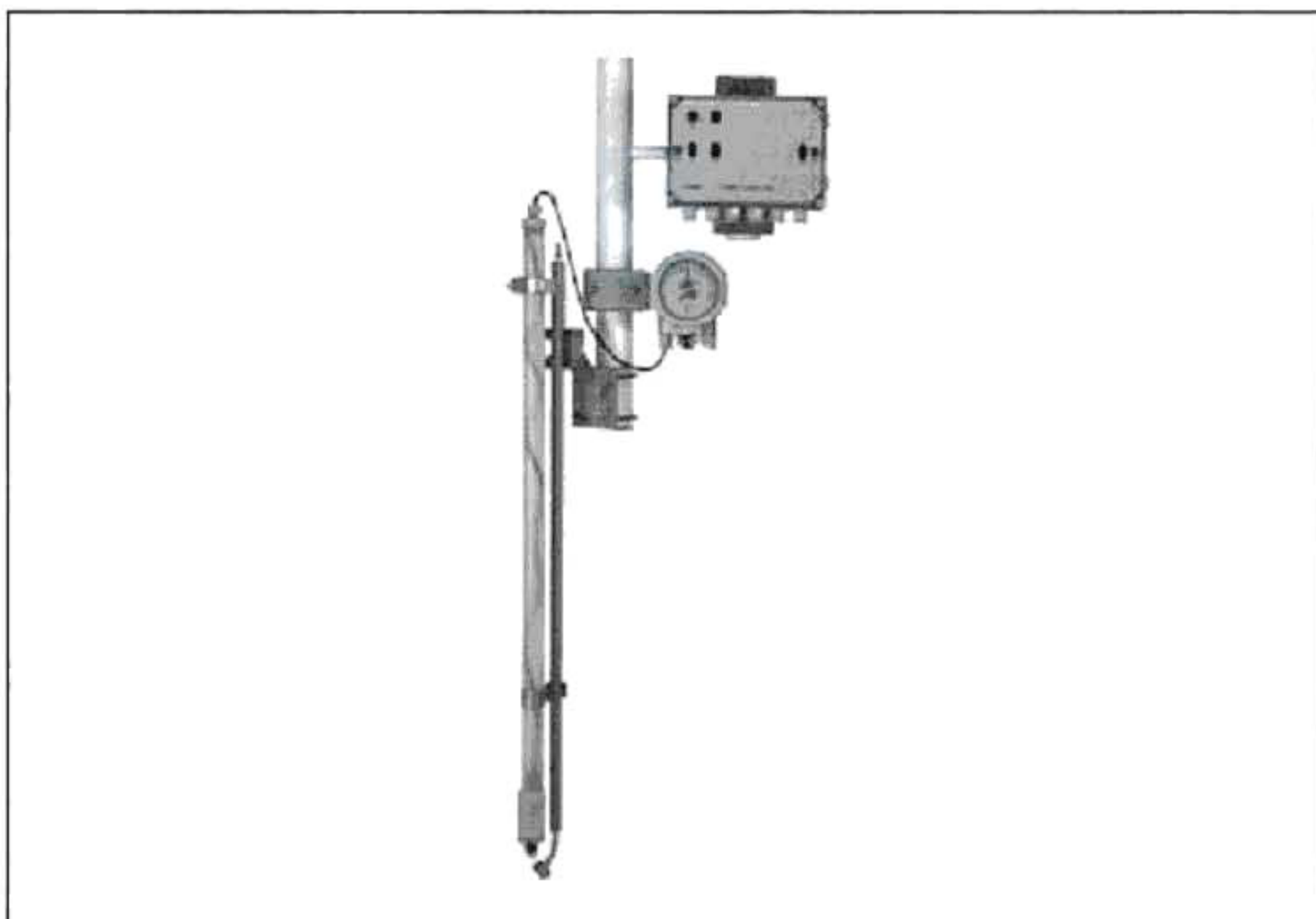


**The more an electrode is manually removed from service, the more it will need to be removed.**

It would seem that the submersion assembly shown in Figure 4-8a would be best for control. However, velocities below 1 foot per second dramatically slow down the electrode measurement response due to the increased boundary layer near the glass surface and promote the formation of deposits, which can further slow down the measurement. The bulk velocity in even the most highly agitated vessels rarely exceeds 1 foot per second and is often much lower. The result is coating problems and a slow response. Removal of a submersion assembly is cumbersome and time consuming because of the long length. Jet nozzles help reduce the number of times the submersion assembly must be removed. Long assemblies in highly agitated vessels require a protective tube with side supports,

The most prevalent electrode installation assembly until the 1990s was a flow through cell chamber or a simple pipe tee into which a probe was threaded. A small sample stream is diverted from the tank or pipeline and





**Figure 4-8a. Submersion Assembly with Jet Nozzle Cleaner (Courtesy of Horiba)**

enters the bottom of the flow chamber and exits out the side as shown in Figure 4-8b. Strainers, filters, jet washers, and ultrasonic cleaners are added to reduce coating problems. Unfortunately, the plugging of strainers and filters can become as much of a maintenance headache as the coating of the electrodes. Winterization of all the fittings and items is difficult and typically lacks the temperature control to keep the sample temperature equal to the process temperature. Today there is a realization that sample systems are undesirable from the viewpoint of the additional transportation delay and increased installation and maintenance costs.

The development of the retractable injector probe shown in Figure 4-8c allowed the insertion and removal of electrodes into pressurized vessels and pipelines. The high velocity in pumped pipelines decreases the coating rate and the time constant of the electrodes. The electrode can be removed, even though the pipeline is pressurized, by slightly loosening the fitting that grips the electrode metal sheath, slowly withdrawing the sheath until it clears the ball valve, closing the ball valve, and withdrawing the sheath the remaining distance. In some respects, this type of assembly is safer than a flow chamber with an integral terminal enclosure because the sealing method is easily checked and any leaks are visible. The restraining strap must never be removed so that the probe does not become a projectile because of worn or missing fittings. A tee and an additional ball valve can be provided for flushing the assembly before



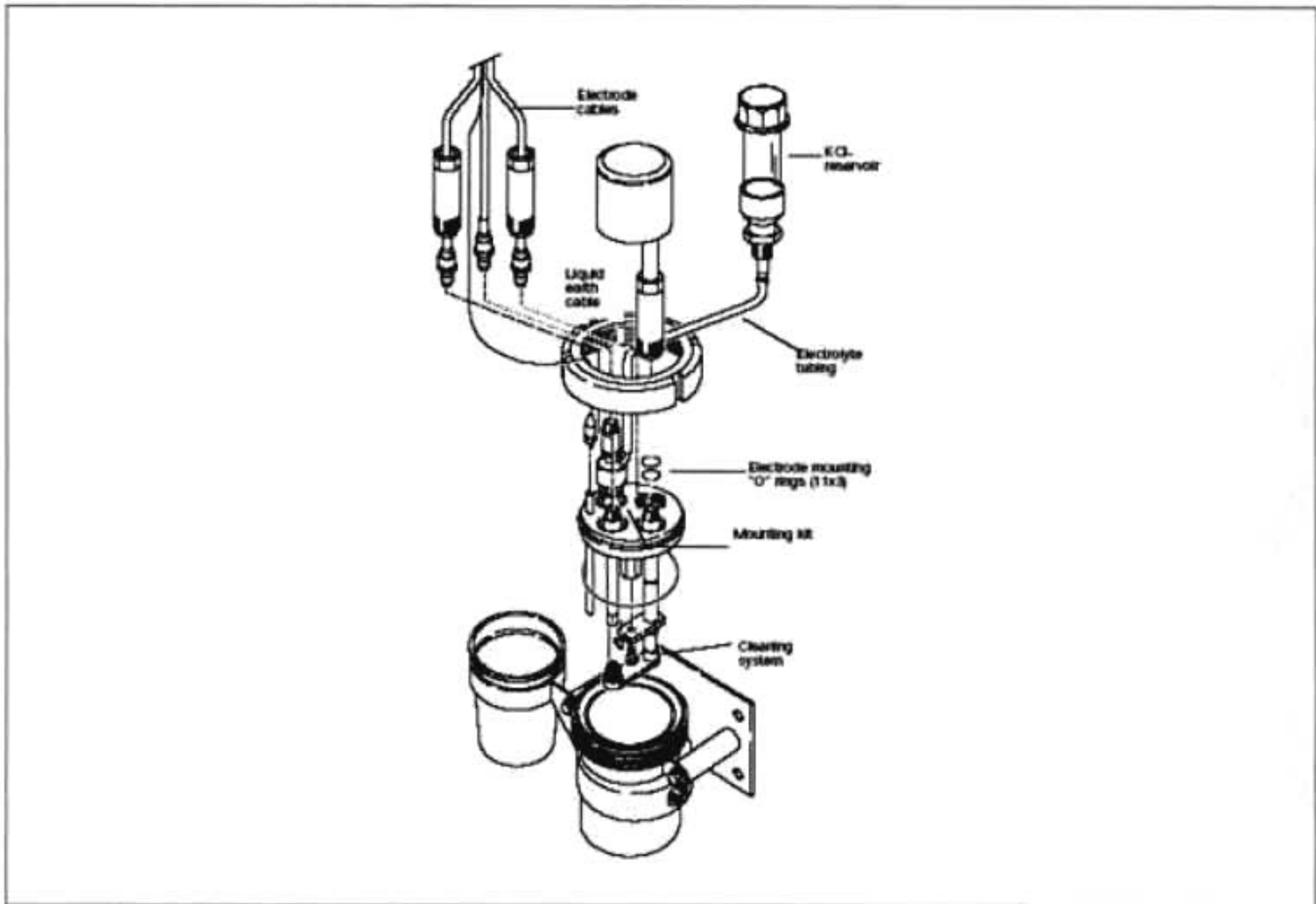


Figure 4-8b. Flow Through Cell with Jet Nozzle Cleaner (Courtesy of Yokogawa)



Electrodes in submersion assemblies, flow through cells, and sample lines tend to have more coating problems and a slower response.



Changes in the sample temperature from winterization and ambient conditions changes the dissociation constants and the solution pH.

removal of the sheath. Fermentors use a sterilizable side entry retractable probe such as that shown in Figure 4-8d.

The best location, except for very abrasive service, is a recirculation line close to the outlet. Installation downstream of the pump is preferred because the strainer will block and the pump breaks up clumps of material that might break the electrodes (Mistake 11 in Figure 1-1e in Chapter 1). The retractable probe provides the most straightforward and economical solution. The electrode tips must be pointed down to prevent the air bubble inside the electrode fill from residing in the tip and drying out the inside surface. An installation angle of  $20^{\circ}$  to  $80^{\circ}$  from the horizontal is sufficient to keep the bubble out of the tip. Some electrode designs



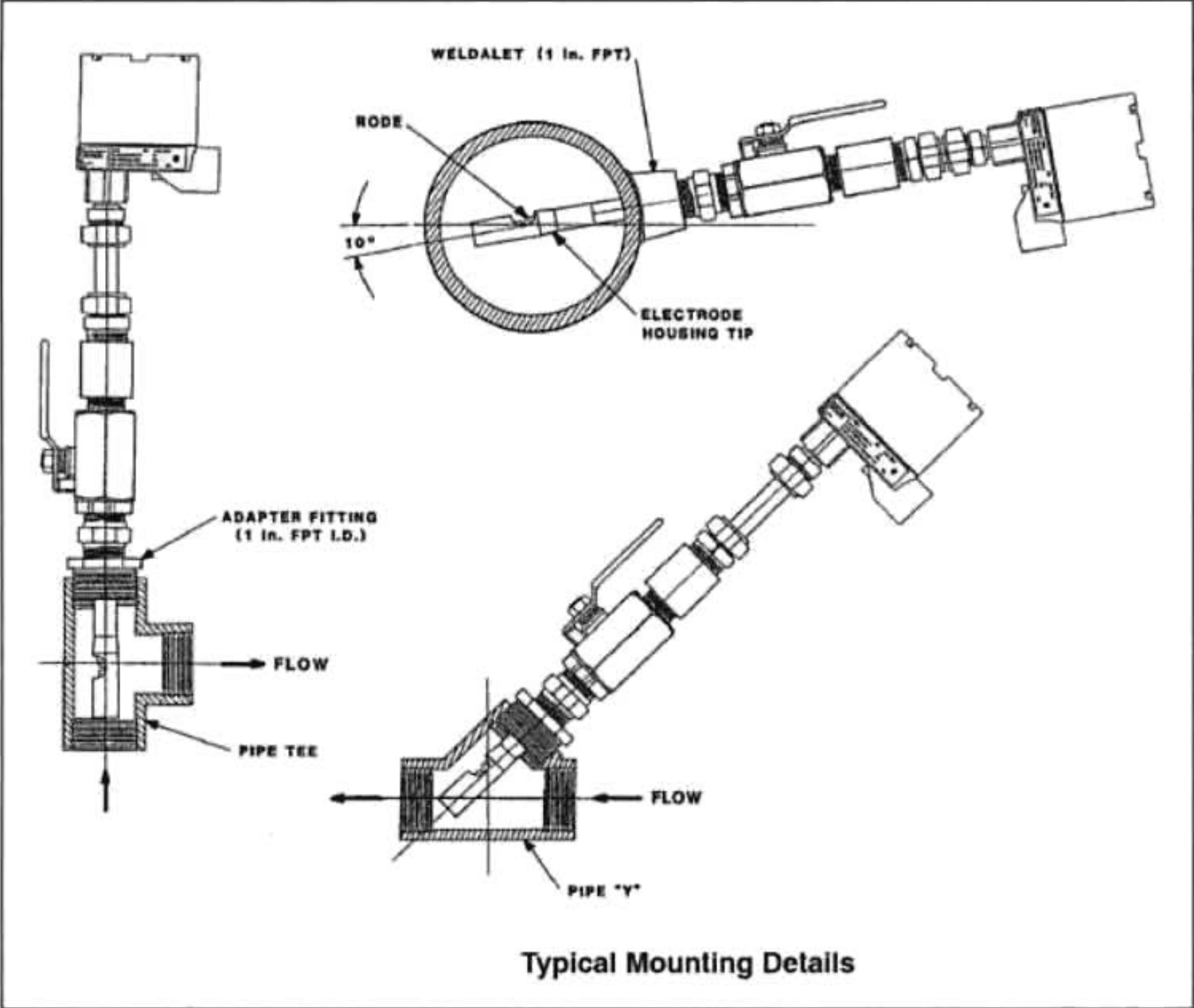


Figure 4-8c. Retractable Probe for Pipelines (Courtesy of Rosemount)

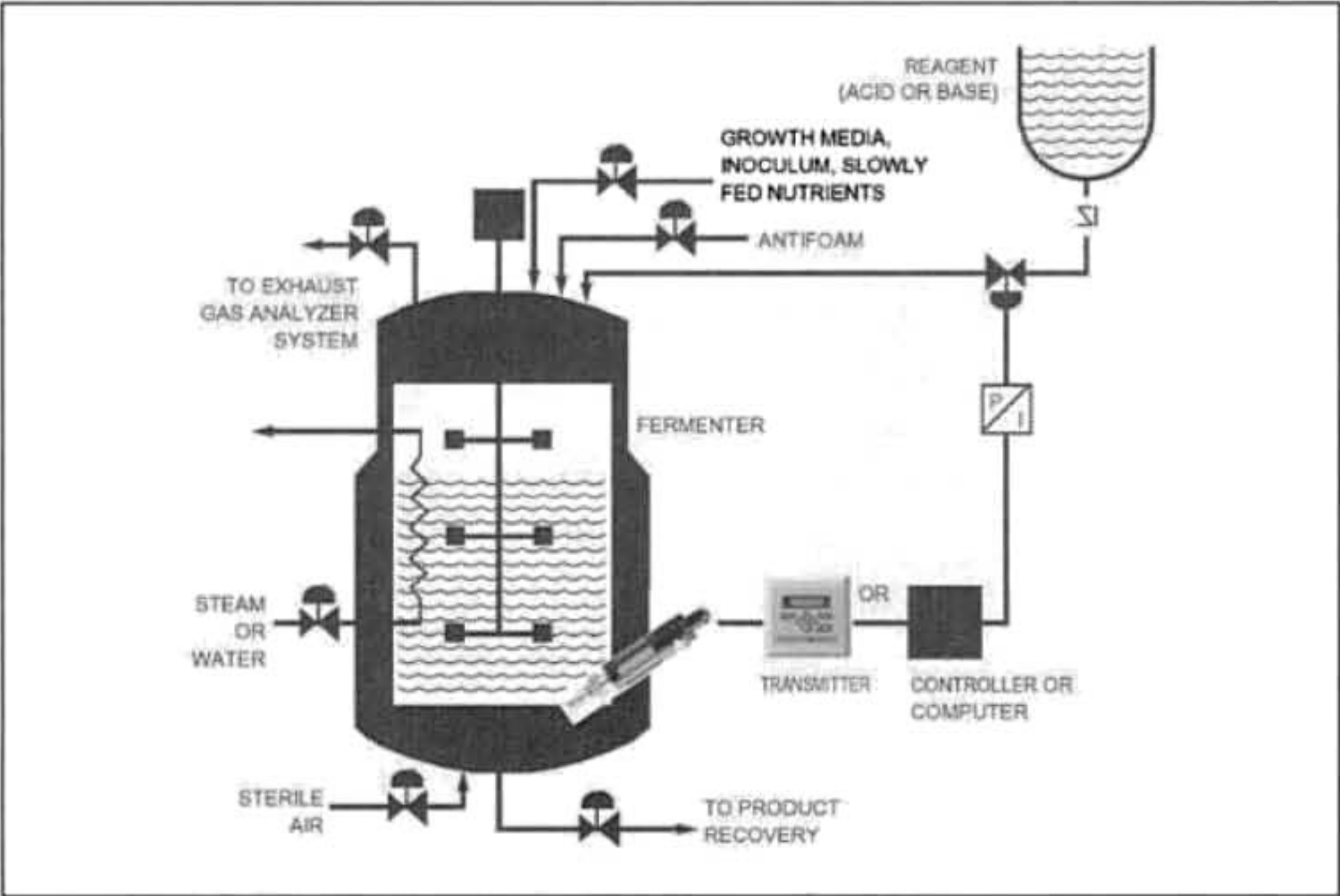



Figure 4-8d. Retractable probe for Fermentors (Courtesy of Rosemount)

eliminate the bubble via a flexible diaphragm for fill contraction and expansion.



Retractable probes in pumped pipelines have cleaner and faster electrodes and open up the opportunity to just leave the probes alone.

Normally retractable injector type probes are installed in a horizontal pipeline unless vertical lines are needed to help drain solids. parallel lines enable probes to be isolated but the velocity and distribution of solids is not equal. Consequently, there tends to be an offset and a difference in life expectancy and coating rate between probes. A series installation of probes ensures each probe sees the same mixture and velocity, which leads to more consistent readings and maintenance requirements. For coating and abrasive service, the slot or hole in the shroud is facing into and away from the flow stream, respectively. For all lines, the velocity is adjusted and in vertical lines, the angle of insertion is varied based on whether the goal is to prevent coatings or abrasion. Figures 4-8e and 4-8f show the arrangements.

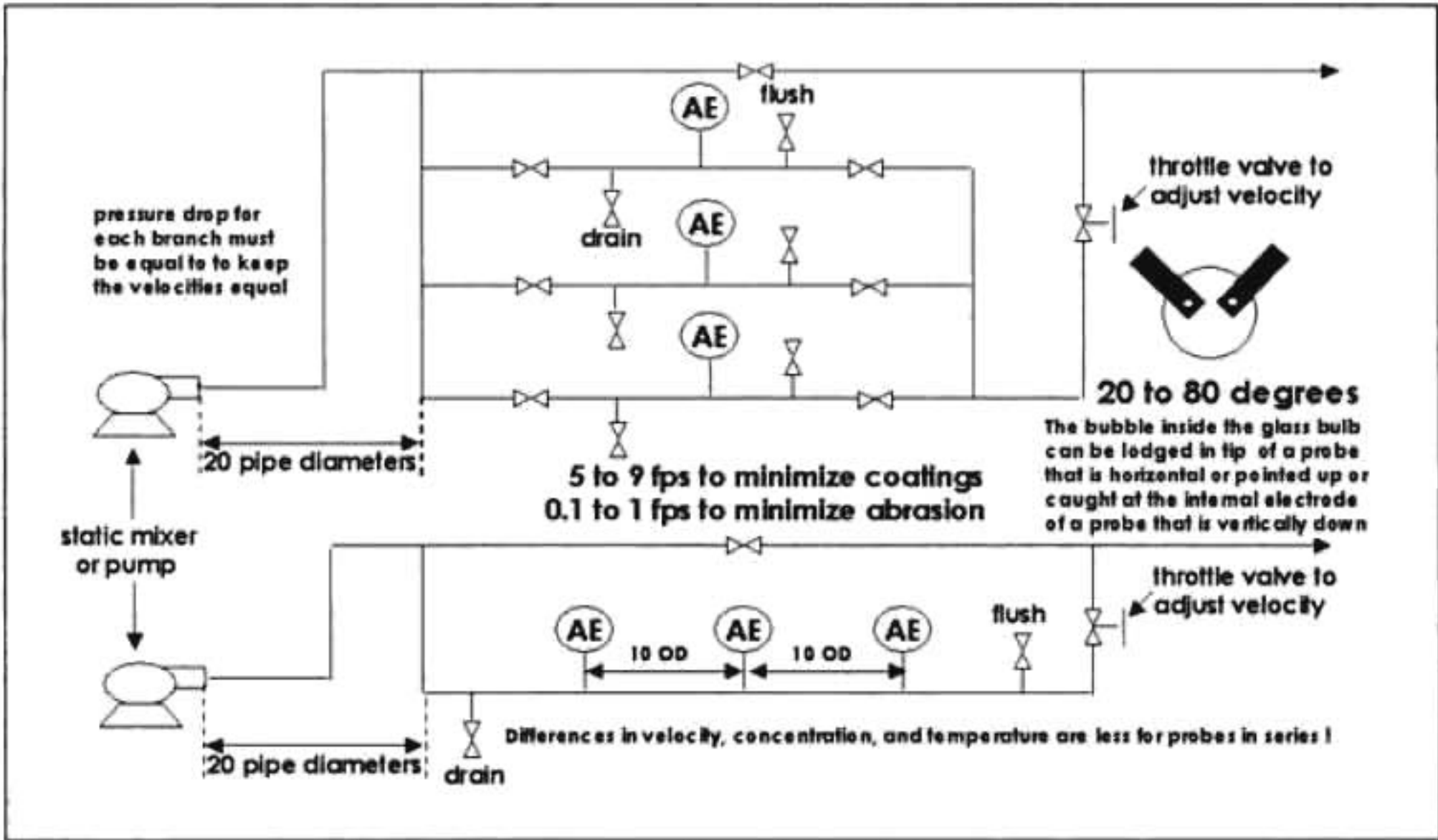


Figure 4-8e. Horizontal Piping Arrangements for Injector Probes

Electrodes do best if they are left in service exposed and in equilibrium with the process. In severe services where the rate of fouling or degradation is excessive, then the electrodes must be periodically removed and serviced. Automated procedures provide much more



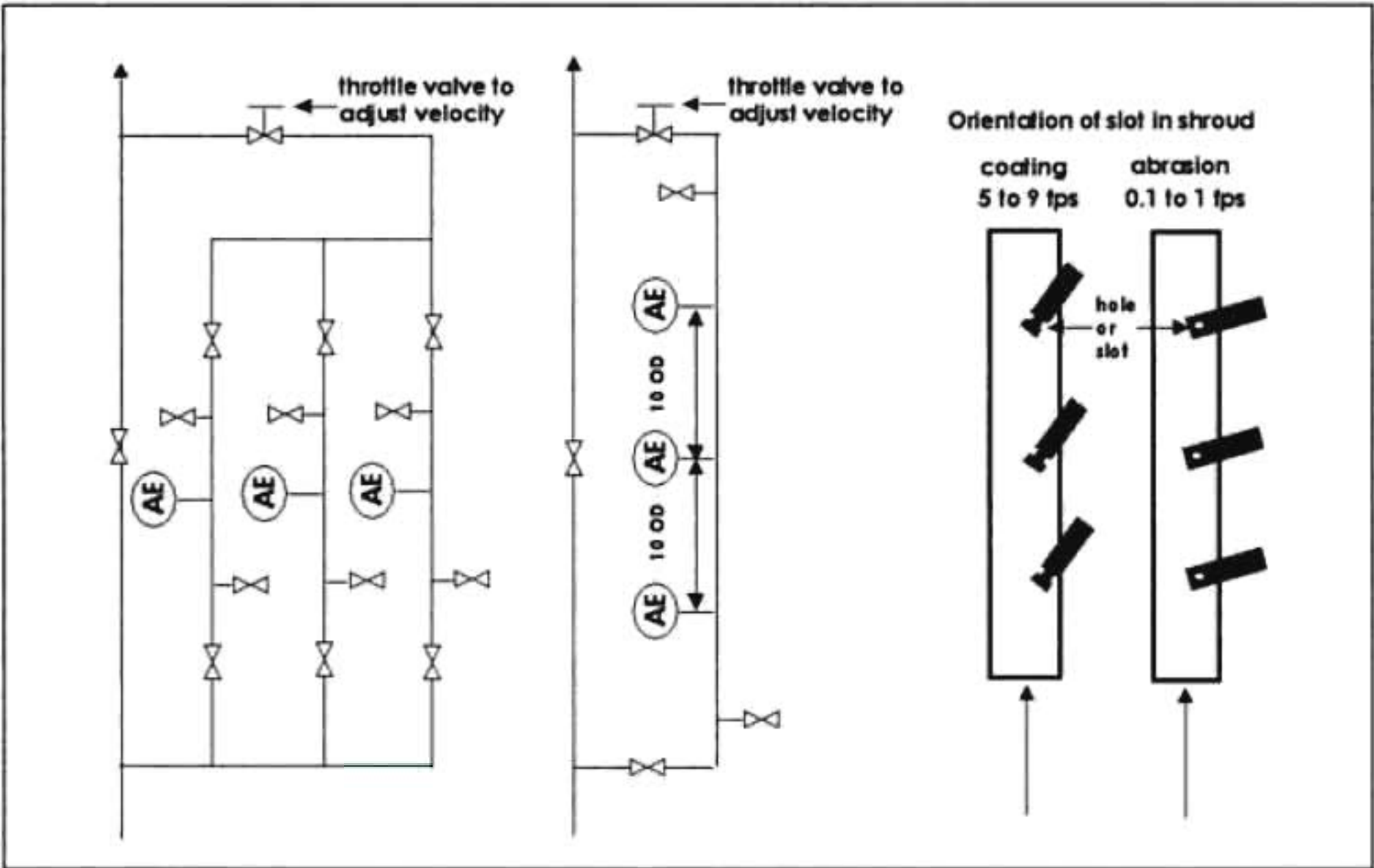


Figure 4-8f. Vertical Piping Arrangements for Injector Probes



A series installation of multiple probes ensures the electrodes will see the same velocity and mixture that is important for consistent performance.

consistent results especially when it comes to pH electrodes. automated retractable assemblies such as that shown in Figure 4-8g have double-acting pneumatic piston actuators that can withdraw and insert an electrode on command by energizing or de-energizing solenoid valves on the supply and exhaust air lines. In the retracted position, the electrode tip sits in a chamber. Solenoid valves on various solutions to the inlet of the chamber are energized to flush, clean, calibrate, and soak the electrode as shown in Figure 4-8h. A solenoid valve on the outlet drains the chamber.



*If velocity cannot keep the electrodes clean or the process exposure time must be reduced or the gel layer rejuvenated, use an automated retractable probe system.*

The following is a compilation of common installation pitfalls:

1. The measurement electrode cable is frayed or its connector is wet (low impedance path to ground is created).
2. The shield to the preamp is grounded (ground loop to solution ground is created).

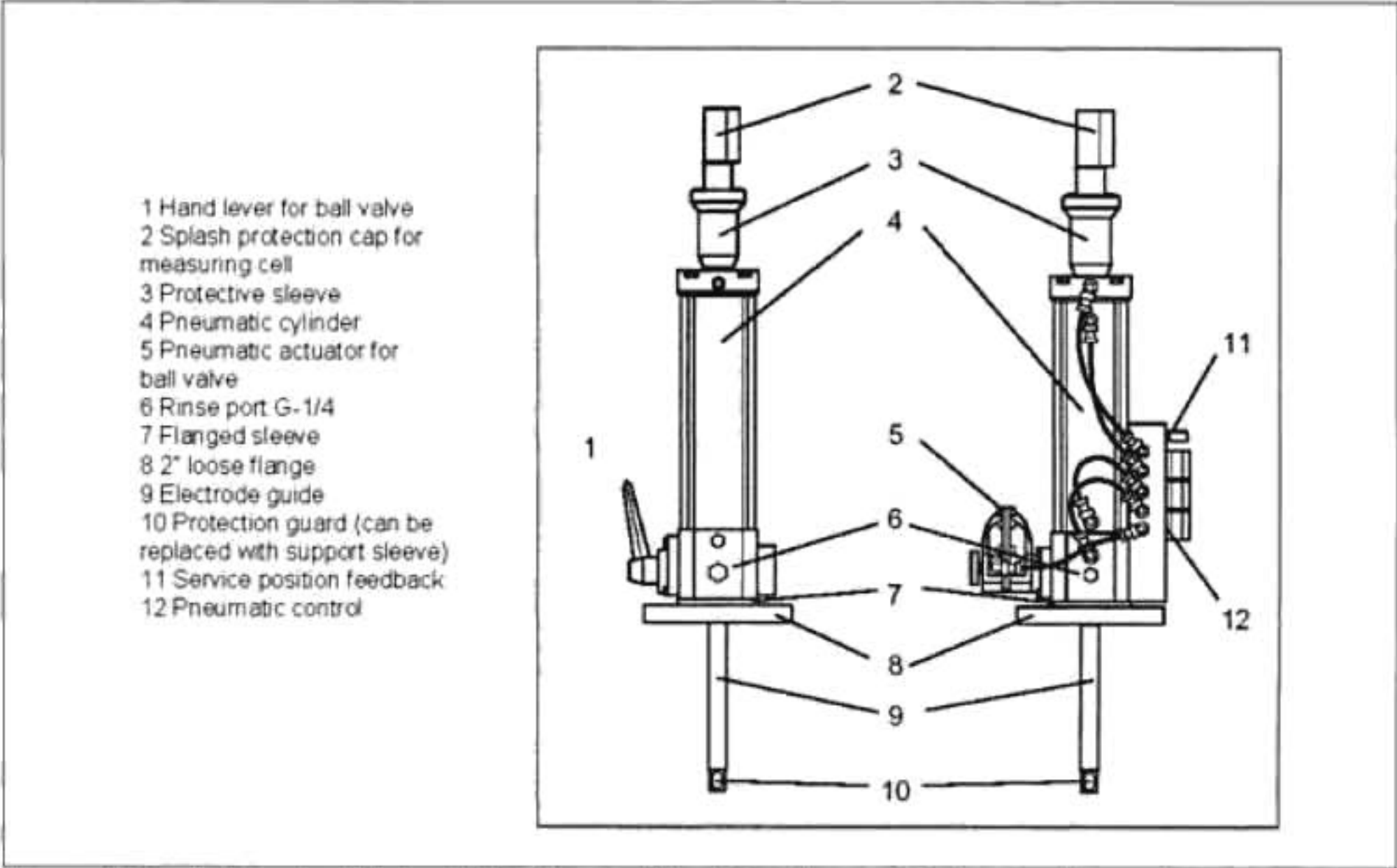


Figure 4-8g. Automated Retractable Assemblies (Courtesy of Endress + Hauser)

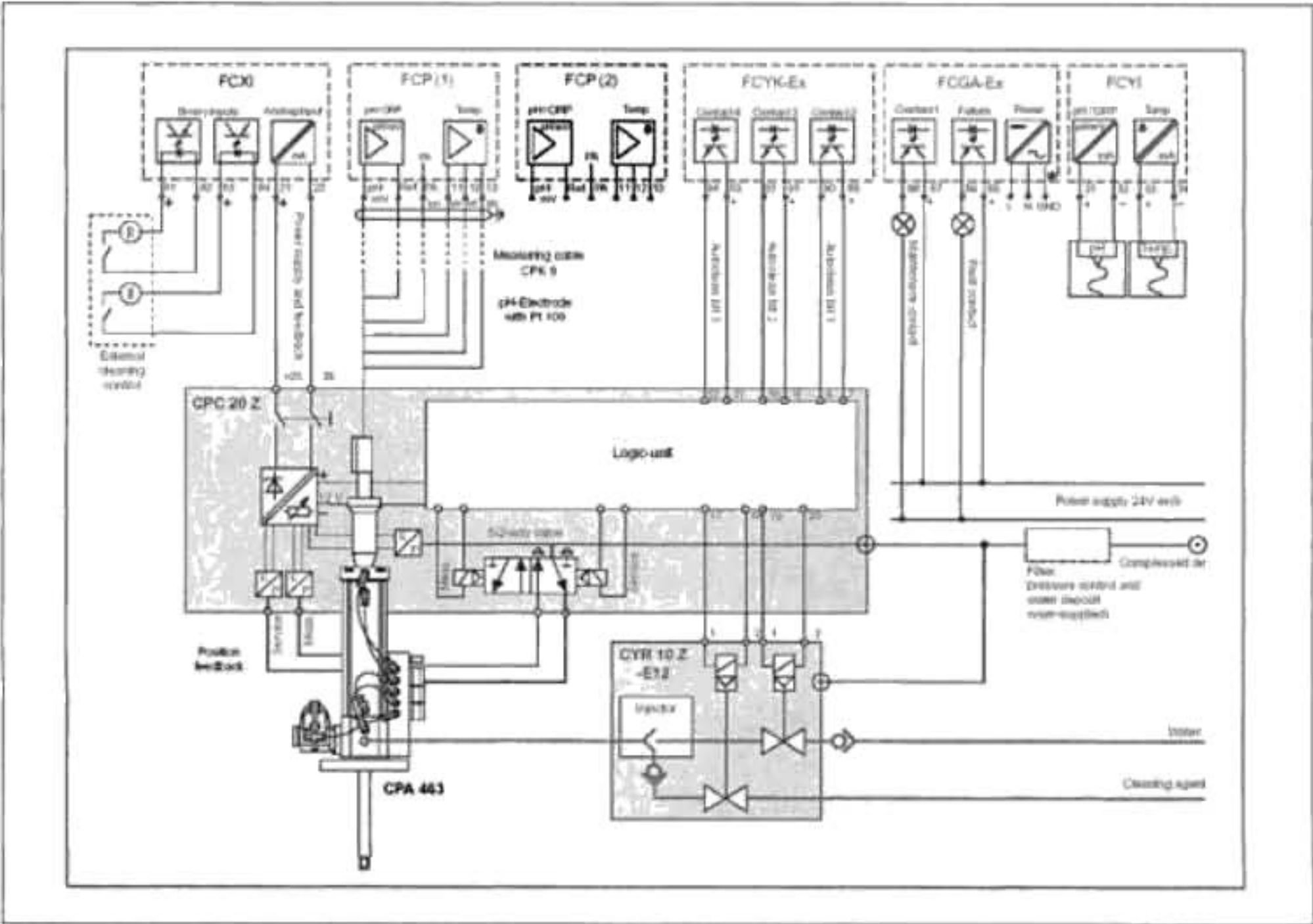


Figure 4-8h. Automated Cleaning System (Courtesy of Endress + Hauser)

3. There is no provision for continuous circulation and self draining of the pipeline or sample line (electrodes sit in stagnant process fluid).



4. A temperature measurement of the process fluid at the electrodes is not transmitted (solution temperature compensation in control room and lab are inaccurate).
5. The sample line is not winterized (sample line freezes during water batching or when the sample flow is shut off).
6. There is no throttle valve and meter for adjusting or measuring velocity at electrodes (partially plugged lines are not detected and optimum velocities are not maintained).
7. The electrode tips are in the top of a line or near the surface of a vessel. (Air bubbles collect near the electrode tips).
8. The slot in the sheath of an injector probe is pointed into the flow for a slurry stream (electrode abrasion develops).
9. The slot in the sheath of an injector probe is not pointed into the flow for a fouling stream (electrode coating develops).
10. The electrodes are not kept wetted for batch or intermittent operations (dehydration of electrode occurs).
11. Submersion electrode assembly is near bottom of vessel and is not supported (assembly breaks due to whipping action from agitation).
12. Submersion electrode assembly is installed in a stilling well (response is sluggish and coating develops due to insufficient velocity past the electrodes).

#### 4-9. Calibration Procedures

In general, electrodes should have a “two point buffer calibration” before they are commissioned and after they are cleaned or the gel layer is rejuvenated. When an electrode has been in service long enough for the reference electrode to reach equilibrium, a “grab sample” process standardization should be done. Thereafter, process standardizations should only be performed when three or more samples preferably spread over several days show the same relative offset to prevent the common problem of chasing calibration adjustments. Samples that come back with alternating error signs are a sure sign of mixing or measurement noise. Chasing noise will cause additional errors besides creating additional work. Data analysis and middle value select of 3 electrodes or 2 electrodes and one estimator can be used to improve the understanding of what is noise and what is real to reduce the frequency of process samples. In the “grab sample” method, the measured pH must be time synchronized with when the sample was taken from the process (not when it was measured in the lab). Also, the sample must be at the same point in the process as the

pH measurement electrode and the lab measurement must be made at the same temperature or corrected to the same temperature in the process as the pH measurement electrode. All of the concerns about the lab sample mixture changing because of absorption, evaporation, dissolution, and reaction discussed in Chapter 3 for titration curves should be addressed.



**Buffer calibrations upset the ionic equilibrium of the reference.**



*After an electrode is in service, a careful process standardization based on long-term offsets is preferred over a buffer calibration unless the electrode must be removed to be cleaned or rejuvenated.*

The transmitter calibration for the electrodes and the output signal to the control room should be checked before installation to verify integrity as received and again before start-up to verify integrity as installed. The electrode and output calibration may not have all the calibration adjustments shown in Equations 4-1m and 4-1o or may use different names. The isopotential pH setting may be referred to as a zero potential or offset adjustment. The standardization setting may be known as a calibration adjustment. The electrode span setting is sometimes done via a slope or efficiency adjustment. The transmitter output span setting is either entered directly or via pH values for 100% and 0% scale. The 0% scale value is sometimes called an *elevation adjustment*.

The standardization and slope adjustments interact for any pH range that does not start at the isopotential point. Thus, these adjustments are repeated until the desired accuracy is achieved. This interaction can be eliminated by the adjustment of the isopotential point.

The basic two point buffer calibration procedure is as follows:

1. Clean the sensor
2. Rinse the electrode with distilled water.
3. Enter the isopotential pH or offset setting.
4. Insert the electrodes into a buffer solution that matches the isopotential pH value and adjust the standardization potential to make it match the buffer. Make sure the buffers are fresh. Use high ionic strength or non-aqueous buffers as necessary to match the process composition and allow enough time for the reference to reach ionic equilibrium. Measure and note the time constant of the measurement electrode response.



5. Rinse the electrode with distilled water.
6. Insert the electrodes in a 4 pH buffer for a set point below 7 pH or in a 10 pH buffer for a set point above 7 pH and adjust the span, slope, or efficiency setting. Make sure the buffers are fresh and a 10 pH buffer has not been sitting exposed to air for more than a few hours. Use high ionic strength or non-aqueous buffers as necessary to match the process composition and allow enough time for the reference to reach ionic equilibrium. Measure and note the time constant of the measurement electrode response.
7. If there is severe interaction between the slope and standardization adjustment, go back to step (4) and adjust the isopotential or offset setting.
8. Store the pH electrode either in a 4 pH solution to condition the gel layer of the glass or a 7 pH buffer to reduce the loss of ions from the reference junction. Electrodes should never be stored in distilled, de-ionized, or pure water because these will cause a high loss of ions from the glass and the reference junction.

#### 4-10. Troubleshooting Logic

Even with combination electrodes, it is helpful to diagnose whether the main problem is with the measurement or reference electrode so the design can be improved. For example, it might be best to change the reference rather than the glass type or shape. If the pH indication has high frequency noise, a slow response, or a shortened span, there is most likely a measurement electrode problem. If the pH indication drifts or develops an offset, it is probably a reference electrode problem. If the offset is very large, the reference electrode is probably contaminated. If you have multiple electrodes, you can swap wires to try different pairs of measurement and reference electrodes to find out which electrodes are the culprits and which combination most closely matches the process sample or buffer pH.



*Spikes, fast noise, slow response, and a shortened span are symptomatic of glass electrode problems whereas drift and an offset are more symptomatic of reference electrode problems.*

Spikes or rapid changes in pH (see Figure 4-10a) are often seen in pH recordings. The user needs to first determine whether the spike represents a real process change. If there are three electrodes and middle value select, the control system automatically ignores unreal spikes. Also, the user can readily infer a spurious change (fast or slow). For a single electrode, the user must figure out how fast a concentration change can occur and then translate from the abscissa to the ordinate of the titration curve to estimate

the possible rate of change of pH. This is not easy and most people don't anticipate how fast pH can change from movement on the steep part of the titration curve.

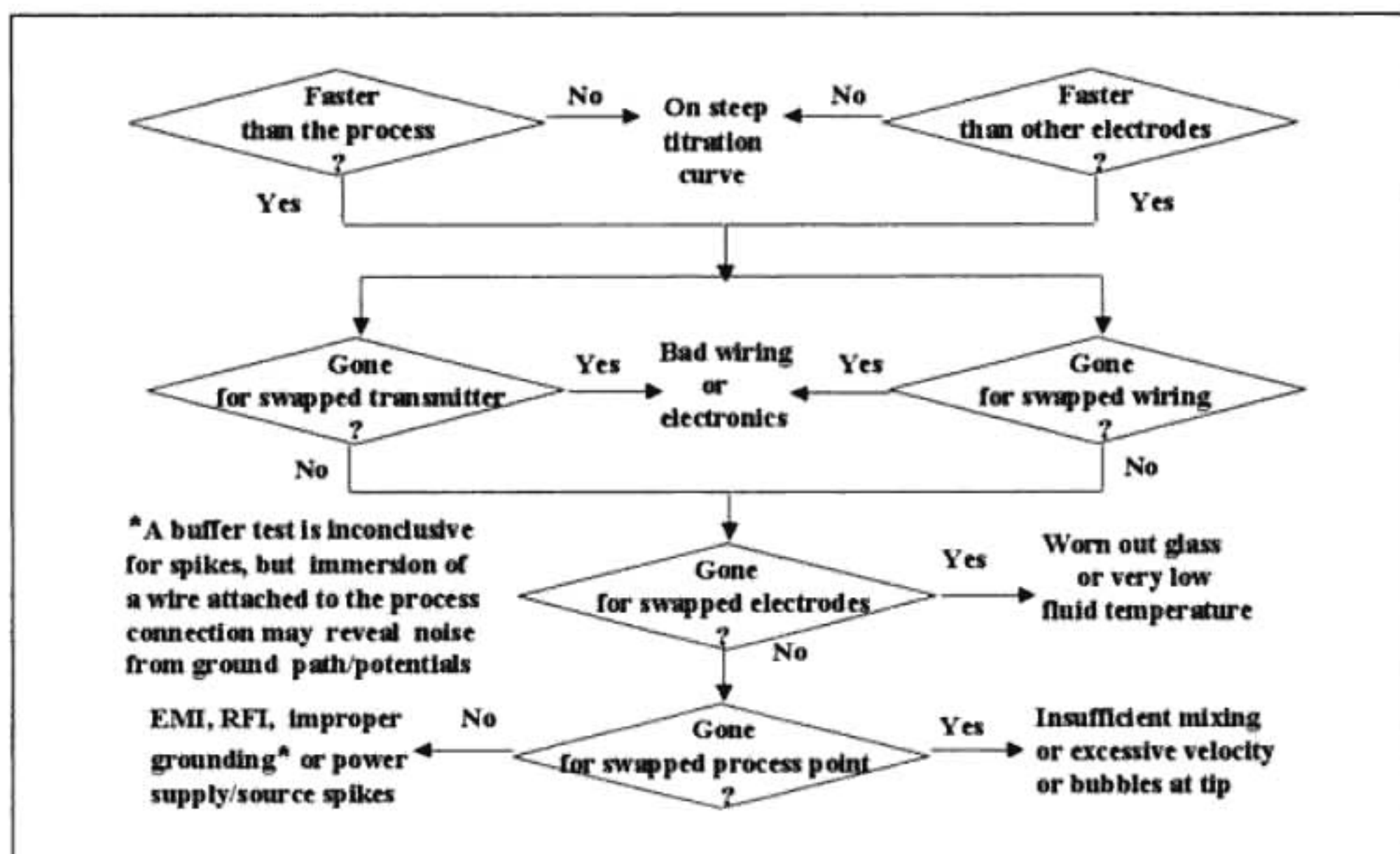


Figure 4-10a. Troubleshooting Logic for Spikes and Rapid Changes

A dehydrated or worn out gel layer or a temperature lower than the glass rating, will cause high glass impedance and a noisy response. A fluctuation of the pH reading from movement of the lead wires by wind or by hand, is an indicator of this condition.

The swapping of transmitters, preamps, and circuit wiring can isolate problems in the measurement circuit but does not rule out grounding or power problems or electrical interference. If a grounded wire inserted into a buffer solution shifts the reading, there is a ground path. This is best done in the field near the actual installation so that the effect of local ground potentials is included.



*To test for ground paths, check if a wire connected to a local ground into the buffer beaker to mimic the solution ground shifts the pH reading.*

The swapping of process connections can help track down the source of the spike to concentration gradients from poor mixing, streaming potentials electrostatic charges from high fluid velocity, or upscale noise from bubbles at the tip of the measurement electrode.



A sluggish pH measurement (see Figure 4-10b) as indicated by an increase in loop period that is not caused by a change in controller tuning is easily tracked down to a coated or broken glass measurement electrode tip, if there are three electrodes and the use of middle select prevents the loop period deterioration. Tough coatings can be removed by briefly soaking or spraying with a dilute hydrochloric acid solution. Glass bulbs should never be manually scrubbed. A buffer test for response time will show the slowness if the coating was not washed off in the preparation for or conduction of the buffer test.

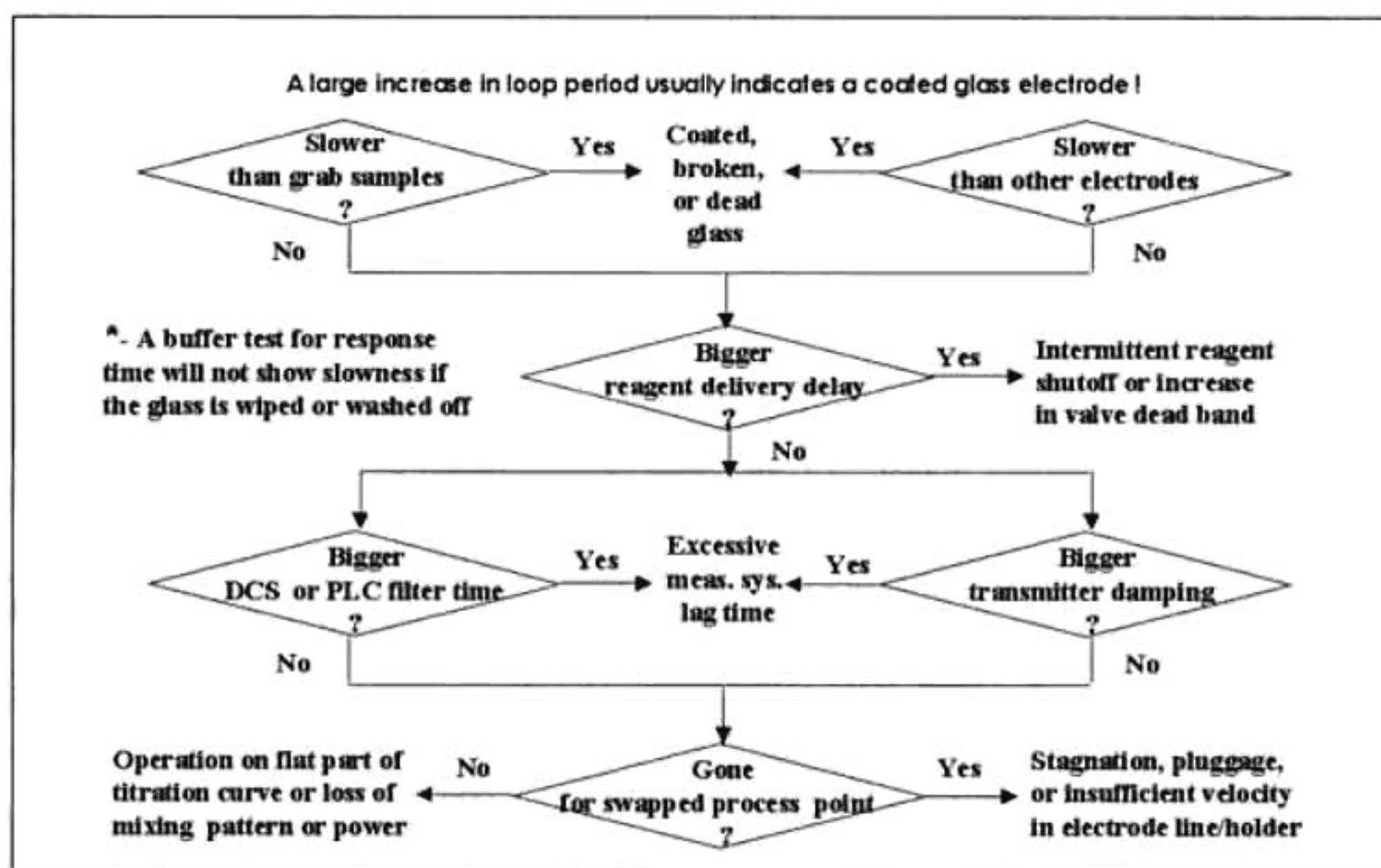


Figure 4-10b. Troubleshooting Logic for a Sluggish Response

If the electrodes are diagnosed to be clean and in good condition, the most common causes are an increase in reagent delivery delay due to intermittent shutoff and thus backfilling of the reagent line per Chapter 6 and an increase in dead time from valve dead band (backlash) and stick-slip (friction) per Chapter 7.

An increase in a filter time in a Programmable Logic Controller (PLC) or a Distributed Control System (DCS) or a damping setting in a transmitter will add a measurement time constant, which contributes to loop dead time and hence, loop period.

The equations developed in the first section of this chapter enable a more sophisticated type of troubleshooting in terms of changes in the pH calibration curve. Performance monitoring systems will eventually be designed to diagnose these systems based on information from smart transmitters and automated cleaning and calibration systems.



Chunks of solids impinging on the electrode, rough handling, chemical attack of glass, or just old age can lead to *cracks in the glass*. If the measurement electrode bulb breaks, process fluid will be in contact with both the inside and outside pH sensitive glass layers. The hydrogen activity, and hence the potential, will be about equal so that the difference in potentials is nearly zero, which corresponds to a constant 7 pH reading. However, the measurement electrode glass resistance is bypassed (paralleled) by a much smaller process fluid resistance so that  $R_1$  decreases and the measured potential increases per Equation 4-1j. The increase in measured potential is seen as a decrease in pH. The result is a shift of the isopotential point vertically upward and a counterclockwise rotation of the millivolt versus pH line to a horizontal position as shown in Figure 4-10a. To determine what the pH reading would be for this position of the line, the original position of the line used in the calibration must be known. For example, if the calibration is represented by the 45° line, the horizontal line in Figure 4-10a at 120 mV would give an indication of 5 pH. Field experience shows that a broken measurement electrode causes a constant pH reading between 4 and 6 pH. If the reference electrode breaks, the internal fill is contaminated with the process fluid. The reference electrode half cell potential will change and shift the isopotential point vertically upward or downward and the pH span will accordingly be biased in the opposite direction. Unlike the measurement electrode, the reference electrode fill can be contaminated without breakage due to its liquid junction. Pulsating pressures or high ion concentrations can force ions from the process fluid through a porous junction into the internals of the reference electrode.

Slurries can cause bulb *abrasion*, non-aqueous fluids or air pockets can cause *dehydration*, and hydrofluoric acid can cause *etching*. The response symptoms for bulb abrasion, dehydration, and etching are the same. In each case, the outer glass layer is less sensitive to hydrogen activity, or, in other words, a given activity will be measured as a lower activity, which corresponds to a higher pH (pH is the inverse logarithm of hydrogen ion activity). The response span is shortened and offset upscale. The outer glass voltage for a given activity and the change in voltage for a change in activity will be less. The isopotential point is shifted left and the millivolt versus pH line slope is decreased by rotation of the line counterclockwise toward the horizontal position. The increase in the glass bulb resistance due to dehydration will cause the isopotential point also to shift vertically downward, which aggravates the upscale shift of the pH span. The response may become noticeably slower and erratic because of the reduced and irregular area for proton exchange between the fluid and the outer gel layer.

Oils, tars, gums, polymers, and particles can cause coating of measurement and reference electrodes. A *partial coating* of the



measurement electrode forms a layer that slows down the diffusion of the hydrogen ions from the process fluid to the glass surface. The result is a very slow measurement response. A *complete coating* of the measurement electrode forms a barrier that stops all diffusion of the hydrogen ions from the process fluid to the glass surface. The result is a constant pH reading whose value depends on the hydrogen activity of the coating. Since the hydrogen activity of most coatings is low, a constant upscale pH reading is common. This corresponds to a horizontal millivolt versus pH line at a negative millivolt level. A partial coating of the reference electrode will change the liquid junction potential and the resistance at the electrode tip. Usually the junction potential decreases and the resistance increases so that the isopotential point is shifted down and the pH span is shifted upscale. A complete nonconductive coating can cause an open circuit between the reference and measurement electrodes. The transmitter output will go off scale up or down, depending on the pH meter manufacturer and model number. The more typical failure mode is upscale.

The presence of a non-aqueous solvent shows up as a pH beyond the normal 0 to 15 pH range. An *acidic solvent* acts as a proton donor so that the proton activity is increased and the pH scale is shifted down. For example, the pH scale for an acetic acid solvent is -6 to -1 pH and for a formic acid solvent is -9 to -2 pH. A *base solvent* acts as a proton acceptor so that the proton activity is decreased and the pH scale is shifted up. For example, the pH scale for an ammonia solvent is 16 to 49 pH. An *alcohol solvent* acts both as a proton donor and acceptor like water so that changes in proton activity are moderated. The pH scale occupies about the same region as water but may extend further upscale and downscale. For example, the pH scale for an ethanol solvent is -4 to + 16 pH. A *hydrocarbon solvent* acts neither as a proton donor nor as an acceptor so that the solvent is passive to changes in proton activity. Consequently, the pH scale upper and lower limits are usually spread further apart than those for water. For example, the pH scale for an acetone solvent is -5 to 20 pH. Often, non-aqueous solvents have a higher resistance than water. So the isopotential point is shifted downscale and the pH span upscale. This shift is counteracted by the more positive liquid junction potential for acid solvents but is accentuated by the more negative liquid junction potential for base solvents. It is important to realize that dehydration, with all its attendant symptoms and errors, will also occur for all non-aqueous solutions unless the measurement electrode is periodically rinsed with water to replenish the hydronium ions in the gel layer. The start of dehydration is marked by a slowing down of the response (an increase in the loop period) and a drift of the measurement upscale. In a control loop, the measurement drift would not be noticeable until a base reagent valve had drifted all the way open or an acid reagent valve had drifted all the



way closed. Thus, the output of the controller should be monitored for the early detection of pH measurement drift.

Pure *water solutions* have a high solution resistance like non-aqueous solutions. The addition of a small concentration of ions changes both the conductivity and pH tremendously, resulting in an erratic measurement besides the upscale shift of the pH span. Most pure water streams will absorb enough carbon dioxide upon exposure to air to exhibit a buffering effect below 7 pH.

Changes in *ionic strength* will cause changes in the liquid junction potential of the reference electrode. If the concentration of positive ions increases, the liquid junction potential increases and shifts the isopotential point up and the pH downscale. If the concentration of negative ions increases, the liquid junction potential decreases or becomes more negative and shifts the isopotential point down and the pH upscale.

Gas *bubbles* can result from gas entrainment from excessive agitation, gas evolution from a reaction, or a gas reagent. The gas bubbles cause a high resistance and reduce hydrogen activity at the measurement electrode upon impact. The result is an intermittent shift of the isopotential point to the left and down, which creates upscale pH noise.

A *short* from the measurement to the reference electrode terminals will cause a 0 mV input and thus a 7 pH reading. In fact, the standby position on some pH meters connects a shorting strap between these terminals to give a 7 pH reading and to prevent polarization of the electrodes during immersion of the electrodes or application of power to the transmitter.

*Moisture* on the measurement electrode terminal, which decreases resistance  $R_3$  in Figure 4-1a, is more of a problem than moisture on the reference electrode terminal, which decreases resistance  $R_4$  in Figure 4-1a. Equations in Appendix G estimate the error that results from the voltage divider effect of moisture on these terminals. For resistances  $R_3$  and  $R_4$  reduced to 10 megohm due to moisture, the error for a 100 megohm measurement electrode is 10% while the error for a 10 kilohm reference electrode is only 0.1 %.

The return of used electrodes is ineffective and raises safety concerns from contamination of the wetted surfaces. It may be impossible to eliminate hazardous chemicals trapped in a porous junction. Also, the washing of the electrodes gets rid of coatings and rejuvenates the glass surface, which severely reduces the scope of the troubleshooting possible by the electrode manufacturer. Most electrode troubleshooting is best done onsite.



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# **Chapter 5: Mixing Equipment**



## Chapter 5

### Mixing Equipment

#### 5-1. What Was Good Might Be Bad

Neutralization systems are generally extremely dilute aqueous streams with set points on a relatively steep portion of the titration curve. Consequently, small deviations in the concentration that might be negligible for most other systems are significant for pH control. For example, a 0.0002% deviation in acid concentration that is 50 times smaller than the 0.01% deviation that corresponds to a uniformity of 99.99% associated with good mixing, would cause the pH to swing between 4 and 10 pH in a strong acid and strong base system per Figure 1-1b in Chapter 1. Most studies in mixing are based on a process gain of 1 since the controlled variable is considered to be the concentration of interest. The logarithmic relationship of pH can create process gains that are orders of magnitude larger. Studies of mixing requirements in pH control systems have typically been conducted for buffered systems, pH set points on a flat portion of the titration curve, and diluted weak reagents. Consequently, they do not reveal the sensitivity and dispersion problem of mixing a few drops of a strong concentrated reagent in a large volume.



**pH control requires a degree of mixing that goes well beyond the norm.**



**A system considered to be well mixed for concentration control may be poorly mixed for pH control.**

The percent concentration deviation of the reagent from its average concentration in a volume should be converted to an equivalent deviation in the reagent to influent feed ratio, which is the X axis of the titration curve. This deviation in ratio should be multiplied by the slope of the titration curve at this point, which is the process gain, to get the deviation in pH. Equation 5-1a shows the definition of the ratio of reagent to influent mass flow. Equation 5-1b shows how this ratio can be computed from the ratios of weight fractions per Equation 2-1i in Chapter 2. The average ratio can be computed for the average concentrations, which gives the operating point on the titration curve. The change in ratio can be

computed from this same equation if the deviation is substituted for the average in reagent concentration in the effluent as shown in Equation 5-1c. The deviation in pH is then this deviation in ratio multiplied by the process gain, which is the slope of the curve at the operating point as denoted in Equation 5-1d. This deviation about the operating point must be well within the control band (minimum and maximum allowable pH) for the system to be considered "well mixed" for pH control.

$$R_{ri} = \frac{F_r}{F_i} \quad (5-1a)$$

$$R_{ri} = \frac{x_{re} * x_{ii}}{x_{rr} * x_{ie}} \quad (5-1b)$$

$$\Delta R_{ri} = \frac{\Delta x_{re} * x_{ii}}{x_{rr} * x_{ie}} \quad (5-1c)$$

$$\Delta pH = \Delta R_{ri} * K_{cv} \quad (5-1d)$$

where:

- $F_i$  = influent mass flow (kgm/hr)
- $F_r$  = reagent mass flow (kgm/hr)
- $K_{cv}$  = process gain for controlled variable ( $\Delta pH / \Delta R_{ri}$ )
- pH = average pH operating point (pH)
- $\Delta pH$  = deviation in pH from average pH operating point (pH)
- $R_{ri}$  = average mass flow ratio of reagent to influent
- $\Delta R_{ri}$  = deviation from average mass flow ratio of reagent to influent
- $x_{ie}$  = average weight fraction of influent acid or base in effluent stream
- $x_{ii}$  = average weight fraction of influent acid or base in influent stream
- $x_{re}$  = average weight fraction of reagent acid or base in effluent stream
- $\Delta x_{re}$  = deviation in average weight fraction of reagent acid or base in effluent stream
- $x_{rr}$  = average weight fraction of reagent acid or base in reagent stream in plant



*For a system to be rated "well mixed" for pH control, the deviation in the reagent to influent flow from non-ideal mixing multiplied by the process gain must be well within the control band.*



## 5-2. Mixing Dynamics

As flows enter and proceed through a back mixed volume from inlet to outlet, molecules on the leading edge recycle back and mix with molecules upstream. In other words, the molecules turned back take longer to exit the volume. The standard deviation of the distribution of residence times of molecules is larger. The folding back smooths out the change in concentration, which translates to a process time constant. In plug flow, eddies and vortices that recycle back molecules are negligible. The result is a sharp transition in concentration and hence pH, which translates to a process dead time. The standard deviation of the distribution of residence times of molecules is nearly zero, which means all the molecules at the leading edge exit at the same time. Plug flow requires radial mixing (mixing over the cross section) to ensure the concentration along the leading edge is uniform. Back mixing requires axial mixing (mixing along the axis of flow).



**Back mixing creates a beneficial process time constant and plug flow creates a detrimental process dead time for pH control.**

For reactions where the time for a reaction to go to completion can approach or exceed the residence time, plug flow is desirable to reduce the residence time distribution to reduce the size of the volume needed for the reaction to go to completion and to improve the yield by reducing byproducts from secondary reactions. In pH systems, the rate of neutralization is so fast that it is complete in less than a second and there are no secondary reactions. Residence time distribution is of no significance for pH control unless there are solids or bubbles that need to dissolve.

A controller has more time to catch up to a disturbance if the change is slow and gradual, which corresponds to a process time constant that is larger than the process dead time. Conversely, a controller has difficulty dealing with abrupt, rapid, and delayed changes from plug flow, which corresponds to a process dead time that is much larger than the process time constant. In Chapter 8 in the loop performance section, it shows how the peak error from a load upset is proportional to the loop's dead time to time constant ratio. The integrated error is the product of this ratio and the dead time, which makes it proportional to the dead time squared. Thus, the magnitude of the dead time can be more significant than the ratio. A small plug flow volume (e.g., a static mixer) with a poor dead time to time



constant ratio but a small dead time can have a smaller integrated error than a large back mixed volume, such as an agitated vessel.

For pH systems, the dead time to time constant ratio determines how far the operating point moves on the titration curve and how much of the nonlinearity is seen by the pH controller. In other words, a small ratio would enable a pH controller to stay close to set point and only be exposed to the change in process gain with curvature in a small operating region. The implication here is that pH control systems will be much more nonlinear for plug flow than for back mixed volumes and linearization techniques presented in Chapter 8 become more important.



**A small plug flow volume may have a smaller integrated error than a large back mixed volume because the process dead time magnitude is smaller.**



***For large volumes, maximize back mixing and minimize plug flow to minimize the error from load upsets and the effects of the pH nonlinearity.***

The residence time is the volume divided by the volumetric throughput flow. For a completely back mixed volume, the residence time becomes a process time constant. For a plug flow volume, the residence time becomes a dead time. Real systems for pH control can be approximated as a combination of plug flow and back mixed volumes. Thus, the residence time is split between a process time constant and process dead time.

A static mixer provides good radial mixing and little back mixing and has a residence time distribution that is close to plug flow. In turbulent flow through a pipe, eddies propel molecules forward and backward so that there is some smoothing in the axial direction but the radial mixing is not as good as the static mixer. In laminar flow through a pipe, there is poor radial mixing and a non-uniform velocity profile. In a vessel with axial agitation, geometry, and feed entry and exit points that prevents stagnation, channeling, or short circuiting, back mixing is promoted and the pH changes are smooth and gradual.

For plug flow, there tends to be more short-term fluctuations (noise) from a lack of smoothing. Consequently signal filtering and middle value selection is generally more important for pH control in a static mixer than in an agitated vessel.





*For plug flow volumes, use linearization techniques, filtering, and middle signal selection to help the pH controller deal with noise and upsets.*

### 5-3. Agitated Vessels

In vessels there are many different internal flow patterns from agitation and many different parameters to quantify the amount of agitation. For pH control, the flow pattern should be axial, as shown in Figure 5-3a in which the fluid is pulled from the top on down near the shaft and circulated out along the bottom to the sidewalls and back up to the top near the sidewalls. If the agitation breaks the surface without froth, its intensity level is in the ballpark for good pH control. The pattern is called axial because of the vertical up-and-down flow pattern parallel to the axis of the shaft. Baffles that are 90° apart extend vertically along the entire length of the sidewall and a sixtieth of the diameter in width are recommended because they help establish the vertical flow currents to reduce vortexing, swirling, and air induction from the surface, as well as increase the uniformity of the flow pattern and assure a more consistent power draw. Tests made with a pitched blade turbine showed that the addition of baffles reduced the time for complete dispersion (mixing time) from 28 to 20 seconds and reduced the standard deviation from 4.8 to 2.4 seconds [Ref. 8.1]. Propeller and pitched blade turbines provide an axial flow pattern. A double spiral blade and a tangential jet nozzle cause a corkscrew axial pattern that is undesirable because the concentration change has a long and slow corkscrew flow path to follow before complete dispersion. A flat blade or bar turbine cause a radial flow pattern (as shown in Figure 5-3b) in which the fluid is pushed and pulled radically out from the axis of the agitator shaft. The radial pattern is undesirable because it results in an area of fluid near the surface that is not mixed as vigorously as required for pH control. A side entry axial agitator will produce the undesirable radial flow pattern at the point of entry. Side entry agitators should be avoided from the standpoint of maintainability as well.



*The agitation in a vessel should be vertical axial pattern without rotation and be intense enough to break the surface but not cause froth.*

For a vessel with axial agitation, baffles, and a liquid height that is about the same as the diameter, the equipment dead time is approximately the turnover time that can be estimated as the liquid mass divided by the summation of the influent, reagent, and recirculation flows plus the agitator pumping rate per Equation 5-3a [Ref. 8.2]. While theoretically the dead time is on the average half of the turnover time, in practice it has been found that time delay is actually appreciably larger than the turnover





*For a vessel with proper geometry, baffles, and axial patterns, the fed batch equipment time constant is 1/5 the mixing time minus the dead time.*

The agitation term “circulation time” is the time interval between consecutive passes of a particle through the impeller. The “circulation time” is less than the “mixing time” and is not a good estimate of the degree of mixing because a particle could be recycled back through the impeller region without mixing with the other regions.

For the traditional batch mode of operation with sequential feed and reagent phases, there is an integrating response since the concentration does not reach a steady state but ramps until a physical limit, such as tank overflow or a high-level interlock is reached. The slope of the ramp divided by the change in the manipulated variable is the integrator gain. This gain depends on the choices of manipulated variable and controlled variable, and the units of both variables. Equation 5-3g gives the integrator gain for a controlled variable that is the reagent acid or base weight fraction and a manipulated variable that is reagent mass flow rate. Since the actual controlled variable is pH, the ramp will slow down and almost appear to stop on a very flat part of a titration curve. The effect of the nonlinear gain will be included in the section on loop performance in Chapter 8 by translating a change in the abscissa to a change in the ordinate of the titration curve. For continuous operation, the abscissa is the ratio of reagent mass flow to influent mass flow. For batch operation, the abscissa simplifies to reagent weight fraction if the influent mass flow addition was completed before the start of the reagent addition and the reagent mass is small relative to the total mass.



**For traditional sequential batch, there is no steady state and the concentration ramp is described by an integrator gain rather than a time constant.**

For continuous operation of a vertical well mixed vessel:

$$\tau_p = \frac{\rho^* V}{F_i + F_r} - \tau_{dp} \quad (5-3e)$$

For fed-batch (simultaneous feed and reagent) operation of a vertical well-mixed vessel:

$$\tau_p = \frac{T_m}{5} - \tau_{dp} \quad (5-3f)$$



For traditional batch (sequential feed and reagent) operation of a vertical well-mixed vessel:

$$K_i = \frac{X_{rr} * F_r}{\rho * V * \Delta F_r} \quad (5-3g)$$

where:

- $F_r$  = average reagent mass flow (kg per minute)
- $\Delta F_r$  = change in reagent mass flow (kg per minute)
- $K_i$  = integrator gain (mass fraction per minute per kg per minute)
- $\rho$  = average fluid density (kg per cubic meter)
- $\tau_{dp}$  = process equipment dead time from mixing (minutes)
- $\tau_p$  = process equipment time constant from mixing (minutes)
- $V$  = vessel liquid volume (cubic meters)
- $X_{rr}$  = reagent mass weight fraction in reagent stream

Even though the dynamic response of an agitated vessel is approximated as the combination of an equipment dead time and time constant, the actual response is S-shaped, as shown in Figure 5-3b for a step change in reagent flow with the controller in manual (open loop). No real process has the sharp transition shown at the end of the dead time, so the theoretical definition of the time constant as the time to 63% of the change after the dead time, while convenient for field estimates, is better visualized via a tangent to the inflection point (point where slope starts to decrease) as shown in Figure 5-3c. The time from the start of the step change to the intersection of the tangent with the initial value is the dead time and the time from the end of the dead time to the intersection of the tangent with the final value is the time constant. In an actual pH trend, the observed open loop response is not just associated with the equipment but is a combination of the equipment, valve, reagent, piping, and measurement dynamics and the titration curve nonlinearity. The subscript 'o' is used to designate the overall open loop time constant seen on the trend to distinguish it from the closed loop time constant used to describe the response of a controller in automatic to a set point.

The entire contents of a vessel can be axial mixed only if the height of the vessel is equal to or slightly greater than the width. For a single impeller, the liquid height should be greater than 50% and less than 150% of the width. This type of vessel will hereafter be referred to as a vertical tank. Equation 5-3a for the equipment dead time is only valid for a vertical tank. If the ratio of the equipment dead time to the time constant is equal to or less than 0.05, the vessel is classified as a vertical well-mixed tank. The importance of this dead time to time constant ratio for controller tuning and control loop performance will be discussed in Chapter 8.

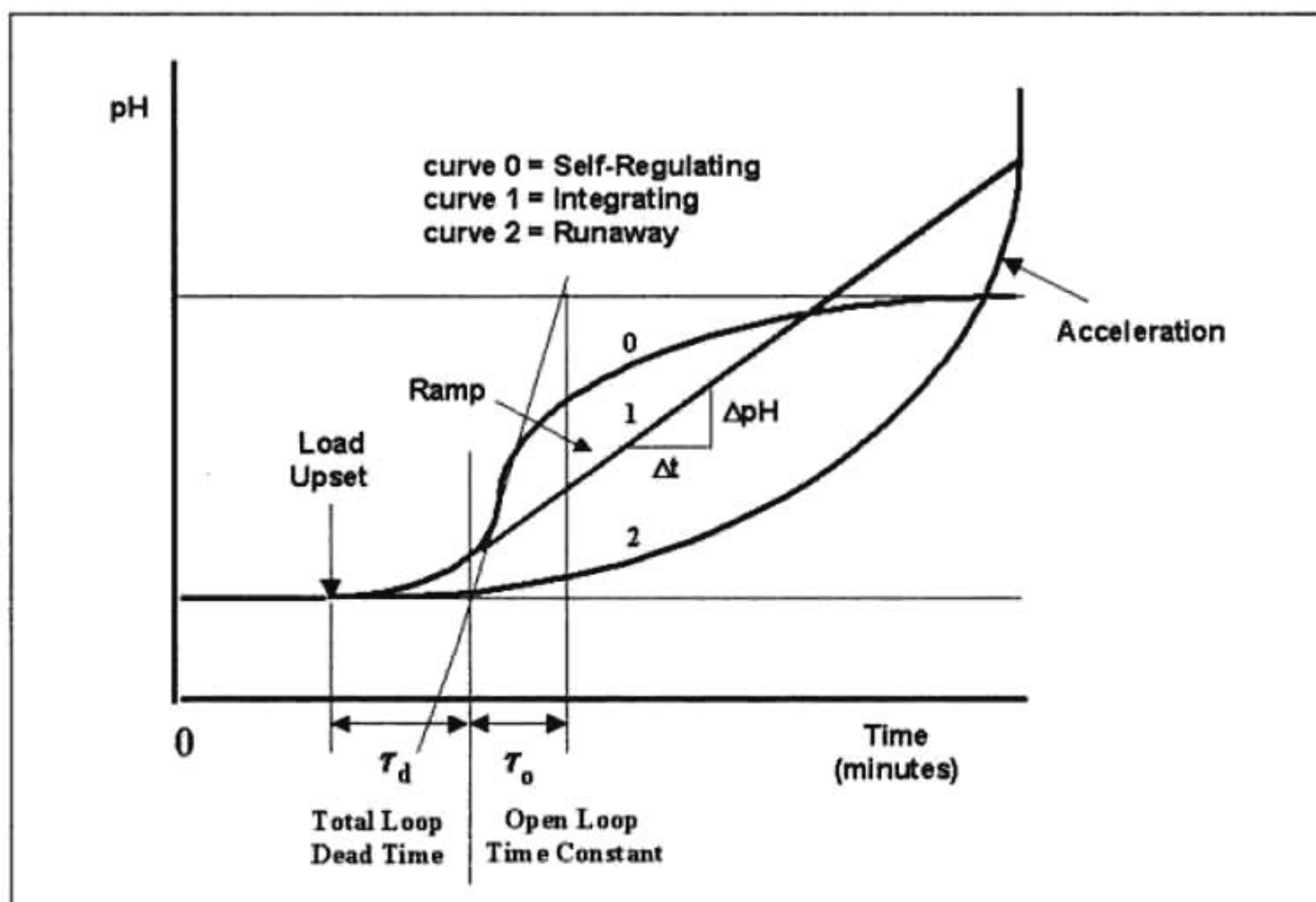


Figure 5-3c. Approximation of the Dead Time and Open Loop Time Constant on a Trend

Horizontal tanks have a length much greater than the height. No matter how many agitators are installed, the complete volume cannot be considered as axially mixed. There will be regions of stagnation, short circuiting, and plug flow. The result of stagnation is a region of fluid whose concentration is slowly dispersed by ion diffusion or migration. The result of short circuiting is a region where a change in the reagent or influent concentration bypasses the rest of the vessel contents and appears in the effluent prematurely. The result of plug flow is a region where the equipment time constant approaches zero and the dead time to time constant ratio approaches infinity. Figure 5-3d illustrates a stagnant region in the far left corner of the horizontal tank from the lack of agitation or an entry flow, a short-circuiting region in the far right corner due to the proximity of the reagent and the effluent nozzles, and a plug flow region of influent to effluent in the middle of the tank caused by radial agitation. For a horizontal tank with proper flow entry and exit locations, the dead time as a percent of residence time proportionally increases with the ratio of length to height [Ref. 8.3]. For example, if the horizontal length is four and eight times the height, the dead time as a percent of residence time would be 20% and 40%, respectively. Equation 5-3h and 5-3i approximate this relationship.





Horizontal tanks are notorious for short circuiting, stagnation, and plug flow that cause excessive dead time and an erratic pH response.

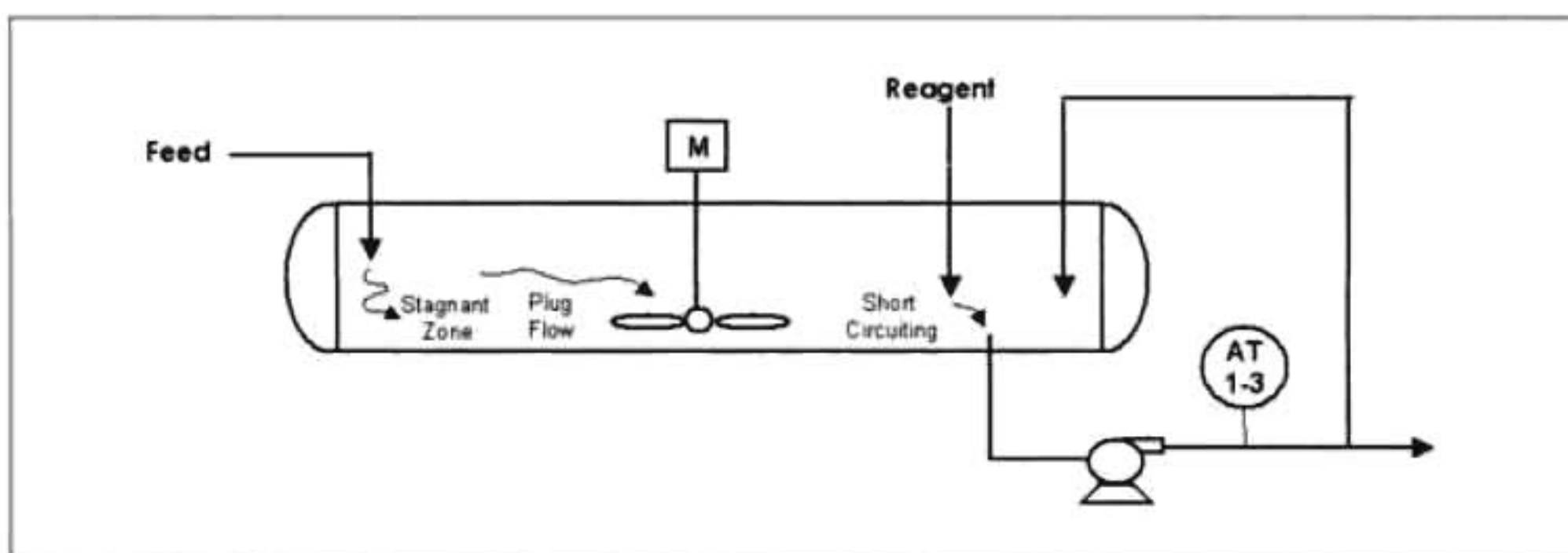


Figure 5-3d. Horizontal Tank with Short Circuiting, Stagnant, and Plug Flow Regions

For continuous operation of a horizontal agitated tank with proper nozzle locations:

$$\tau_{dp} = \frac{\rho * V}{F_i + F_r} * (L/H) * K_z \quad (5-3h)$$

$$\tau_p = \frac{\rho * V}{F_i + F_r} * [1 - (L/H) * K_z] \quad (5-3i)$$

where:

- $F_i$  = influent mass flow (kg per minute)
- $F_r$  = reagent mass flow (kg per minute)
- $H$  = liquid height (meters)
- $K_z$  = geometric factor (0.05)
- $L$  = vessel length (meters)
- $\rho$  = average fluid density (kg per cubic meter)
- $\tau_{dp}$  = process equipment dead time from mixing (minutes)
- $\tau_p$  = process equipment time constant from mixing (minutes)
- $V$  = vessel liquid volume (cubic meters)



*For a horizontal agitated vessel, the dead time as a portion of the residence time is proportional to the ratio of vessel length to liquid height.*

Even if a vessel does not have a control loop on it, it can still play a critical role in the attenuation of oscillations. The time constant of a vessel is effectively the filter time in Equation 5-3j, which is an approximation for

For a single vessel volume:

$$A_o = A_i * \frac{T_o}{2 * \pi * \tau_p} \quad (5-3j)$$

where:

$A_i$  = amplitude of input oscillation into volume (reagent to influent ratio)

$A_o$  = amplitude of output oscillation from volume (reagent to influent ratio)

$T_o$  = period of oscillation (minutes)

$\tau_p$  = process equipment time constant from mixing (minutes)

If the vessel is upstream of a control loop, it can dramatically reduce reagent use by attenuating oscillations of influent concentrations and provide cross neutralization of streams. If these are related to batch operations or the start-up and shutdown of unit operations, the vessel size required may be extremely large. For example if the batch cycle time is 2 hours, the effective oscillation period would be 4 hours. However, the cost of operating the tank may be low because agitation may not be necessary if there is no layering of liquids or settling of solids from low velocities. Vessels or volumes with residence times of days do not need to be agitated to provide a beneficial filtering effect because there may be sufficient smoothing just from ion migration. For example, even if the back mixed portion of the residence time is only 20% from feed and recirculation flow, the time constant for a unagitated vessel with a 24 hour residence time would be 4.8 hours and would be able to noticeably filter a batch cycle time of 2 hours. Thus, large tanks laying around in a salvage yard may offer a big opportunity to reduce reagent cost.



**An unagitated vessel with a pH control loop can be turned from a terrible loser into a big time winner by moving the loop upstream or downstream.**

If the vessel is downstream of a control loop, it can smooth out the oscillations from load upsets and stick-slip. For a reasonably well tuned



loop, the period for an oscillation whose amplitude is decreasing (damped) is about twice the ultimate period or 4 to 8 times the total loop dead time per equations presented in Chapter 8 on controller tuning. The period of the equal amplitude oscillations (limit cycle) for stick-slip is longer and increases as the controller is detuned in an attempt to kill it.

For a well-designed static mixer, the total loop dead time should be about 6 seconds, which means a time constant of just 24 to 48 seconds can provide noticeable smoothing of a damped oscillation and may be achieved by a wide spot in the line, such as an extra large concentric pipe around the original pipe with holes to act as sparger and increase the back mixing. For a vertical well mixed vessel with a total loop dead time of 1 minute, a back mixed time constant of 4 to 8 minutes downstream would appreciably attenuate a damped oscillation. The installation of pH measurements or dynamic online pH estimators on the discharge of downstream volumes can soothe concern and instill confidence in the performance of the system by showing how much the oscillations have been smoothed. This is particularly important for static mixers because the pH measurement will be noisy and have a propensity to oscillate severely because of the lack of back mixing. In fact, it will be shown that an inline pH loop that controls the filtered average of horrible sustained oscillations for a strong acid and strong base system can draw a straight line in the discharge of a very large downstream volume. As a minimum, it can greatly reduce pH constraint violations. For example, the historical trend of pH on a vessel downstream of a static mixer can eliminate instantaneous hazardous waste limit violations.



**pH measurements or dynamic online pH estimators on a downstream volume can reveal that the pH loop is actually doing a great job.**



***Use a large volume upstream to reduce reagent use and a relatively small volume downstream to reduce pH constraint violations.***

## 5-4. Static Mixers

Static mixers have motionless internal elements, as shown in Figure 5-4a, that subdivide and recombine the flow stream repeatedly and cause rotational circulation of the flow stream to provide radial mixing of the stream, but very little axial or back mixing. Consequently, fluctuations in pH over the cross section are smoothed, but fluctuations in pH with time, which are axial, show up unattenuated in the discharge as shown in Figure 5-4b. The equipment dead time is about 80% of the residence time for a static mixer and most manufacturers are working toward making their static mixers exhibit plug flow to reduce the residence time distribution [Ref. 8.4]. While this is beneficial for many chemical reactions, it makes the discharge pH more likely to spike and violate constraints.

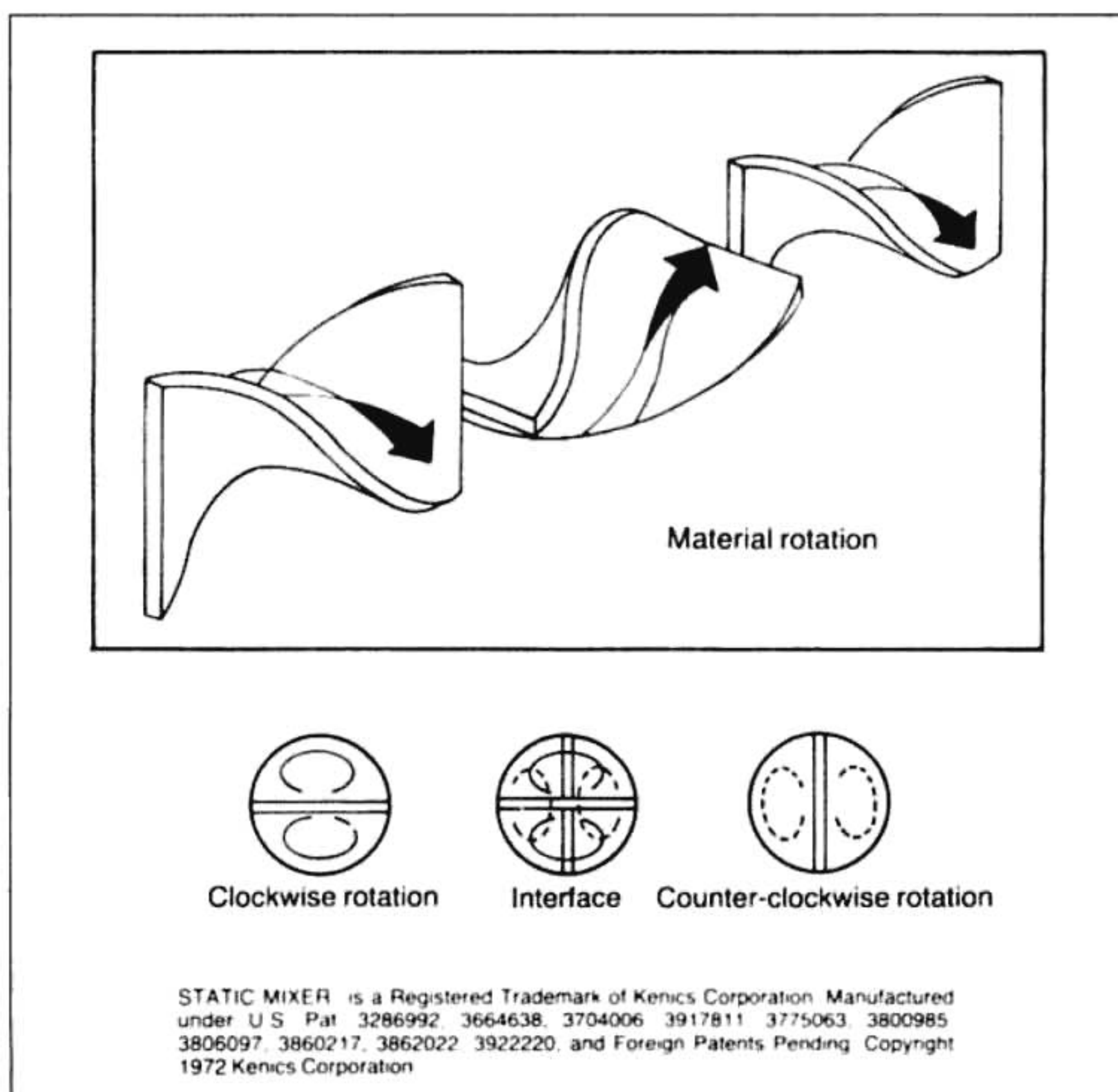


Figure 5-4a. Motionless Internal Elements of a Static Mixer that Subdivide the Flow



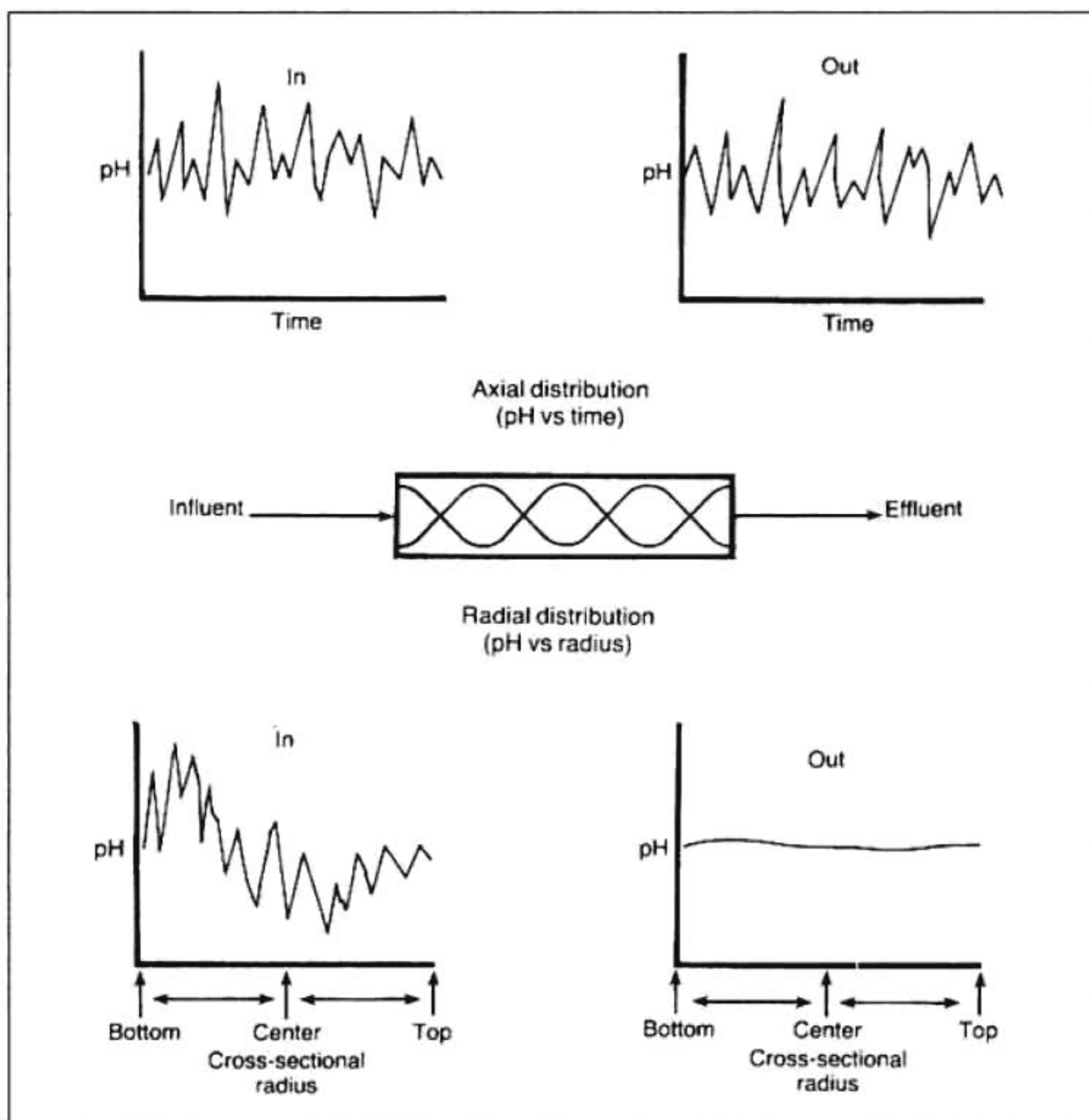


Figure 5-4b. Good Radial Mixing but Poor Axial Mixing of a Static Mixer



Oscillations and noise will pass through a static mixer unattenuated and the poor dead time to time constant ratio leads to more oscillations.

Flow pulses from a positive displacement reagent pump and drops associated with a high viscosity reagent or low reagent velocity will not be back mixed and will cause a noisy pH signal. Bubbles from a gaseous reagent will also cause a noisy pH signal because the residence time is not sufficient for complete reagent dissolution. The use of additional motionless elements beyond the normal number does not usually increase drop or bubble dispersion as much as an increase in stream velocity by a decrease in static mixer diameter. While a static mixer has a poor dead time to time constant ratio that tends to make a pH loop oscillate, it offers

a significant advantage of a small magnitude of dead time and a small volume of off-spec material from a load upset. This will be discussed in greater detail in the control system selection section of Chapter 8.



**The extremely small residence time of a static mixer greatly reduces the magnitude of the dead time and the volume of off-spec material.**

About 100 equivalent pipe diameters of turbulent flow will provide about the same degree of radial mixing as a static mixer. However, the equipment dead time is several times larger because of the larger volume needed to get a sufficient number of diameters. The length of piping between the reagent injection point and pH measurement point, and hence the transportation delay, can be reduced by the use of fittings and valves that have a large number of equivalent pipe diameters.

## 5-5. Sumps, Ponds, and Lagoons

As the width or length of an agitated sump increases with respect to its height, the quality of agitation moves from that for a horizontal tank to that for a pond or lagoon. The equipment dead time will increase from 40% to 80% of the residence time. A pond or lagoon will have an equipment dead time that increases with size from 80% to 99% of the residence time. There will be stagnation areas that change with the amount of sunshine and wind. Submerged static mixers with air jets and submerged turbine agitators can provide localized back mixing [Ref. 8.5]. While the portion of the residence time that is dead time is decreased, the magnitude of the residence time, and hence the dead time, is still enormous. The detrimental effects of such a large dead time on controller tuning and performance will be detailed in Chapter 8. However, pond and lagoon volumes can provide tremendous smoothing of oscillations by dilution and ion migration. However, this is rarely considered in determining the hazardous waste violations of surface impoundments.



***pH control loops should not be installed on sumps, ponds, and lagoons but on a static mixer or vertical well mixed vessel upstream or downstream.***



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## Chapter 6

### Control Valves

#### 6-1. A Moving Story

Stick and slip occurs whenever the valve needs to move even if it is in the same direction. Even after it moves, it cannot move again unless the change in signal is greater than the stick. When the valve does move, it jumps or slips by an amount that is usually larger than the change in signal. Stick and slip generally occur together and have a common cause of friction in the actuator design, stem packing, and seating surfaces. Rotary valves with high temperature packing and tight shutoff (the so-called high performance valve) exhibit the most stick-slip. Rotary valves tend to also have shaft windup where the actuator shaft moves but the ball, disc, or plug does not move. It is much worse at positions less than 20% where the ball, disc, or plug is starting to rotate into the sealing surfaces. For sliding stem (globe) valves, the stick-slip increases below 10% travel as the plug starts to move into the seating ring. These problems are more deceptive and problematic in rotary valves, because the smart positioner is measuring shaft position and not the ball, disc, or plug stem. Here is the rub—if there is stick-slip, the controller will never get to set point and there will always be a limit cycle. The biggest culprits are low leakage classes and the big squeeze from graphite and environmental packing, particularly when they are tightened without a torque wrench. A bigger actuator may help but does not eliminate the problem. An undersized actuator can cause a huge additional slip. Stick-slip of 20% often occurs at breakaway from the seat of high performance valves and for any valve at any position with Graphite packing and no positioner. Even with a positioner, stick-slip of 4% has been commonly observed for high friction packing [Ref. 6.1].



*To provide isolation, use a separate on-off valve and avoid the specification of tight shutoff and high performance valves for throttling reagent.*

Whether you can see them or not the oscillations from control valves are everywhere in the process [Ref. 6.2 and 6.3]. It is just a matter of how large and how important. When the amplitude is less than the exception reporting setting of controllers, data highways, and historians, the oscillations do a disappearing act on operator displays and trends [Ref. 6.1]. All control valves have a resolution limit determined by the amount of stick-slip shown as the stair case in valve position as the valve first starts to open in Figure 6-1. In the best throttling valves with air actuators, the stick-slip is normally only about 0.1% and its effect is not observable in



the trend recordings of most control systems. This chapter will discuss how this seemingly minor limitation in the resolution of the control valve will clearly show up as a large sustained oscillation for a set point on the steep portion of the titration curve because of the high process gain. Thus, the extreme sensitivity of the pH process requires a valve resolution that goes well beyond the norm and pH control systems are the best test for the stick-slip in a control valve. The number of stages of equipment needed for neutralization may be dependent on the capability of the control valve. It is difficult to effectively use more than one control valve per stage. To get a control valve whose limit cycle from the valve resolution limit is within the control band, an extremely small and precise control valve is necessary. To achieve the large range of reagent addition and extreme precision required, several stages are used with the largest control valve on the first stage and the smallest control valve on the last stage. This chapter will show how to estimate the rangeability and resolution requirement for a reagent valve based on the distance from the influent pH to the set point and slope of the titration curve at the set point.



**Set points on the steep portion of a titration curve necessitate a reagent control valve precision that goes well beyond the norm and offers the best test to determine a valve's actual stick-slip in installed conditions.**



**Reagent valve stick-slip may determine the number of stages of neutralization required, which has a huge impact on a project's capital cost.**

The dead band in a control valve does not determine the resolution limit directly but adds dead time in the response that is particularly significant for the slow pH response of large volumes and operating points on the flat portions of titration curves. Dead band occurs only when the valve needs to change the direction of its stroke; thus dead band is how much the signal must change direction to reverse the stroke direction. The official test is done for a full-scale stroke in both directions as shown in Figure 6-1 but dead band occurs for any stroke whenever the direction is reversed. It is caused by lost motion commonly associated with backlash from actuator shaft and stem connections and linkages. It is worse for rotary valves because of the gaps in gear teeth in rack and pinion and the slot in scotch yoke actuators, key lock shaft-stem connections, and linkages to transfer vertical actuator shaft motion to rotary ball, disc, or plug movement. Dead bands of 8% have been commonly observed for such



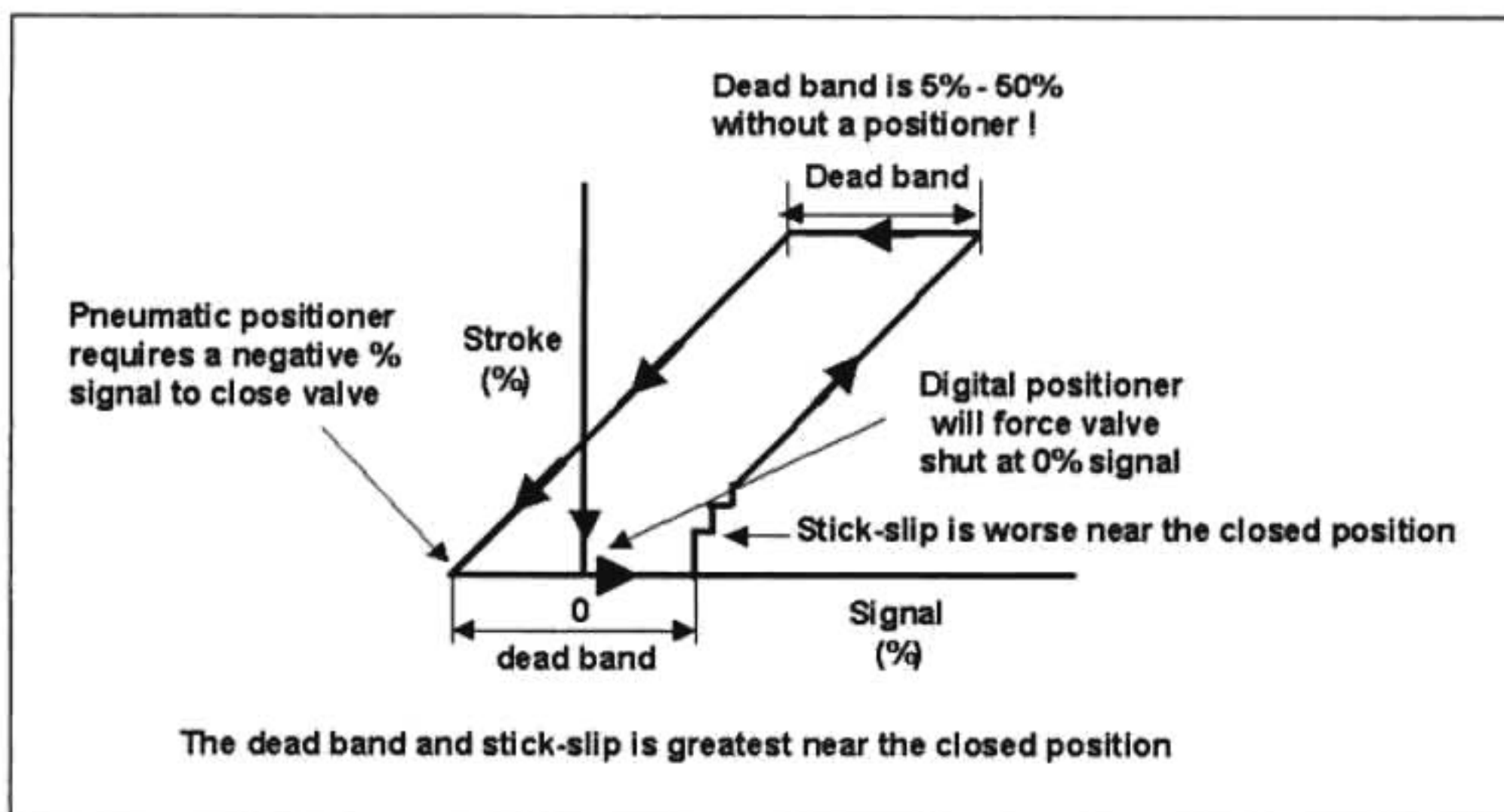


Figure 6-1. Control Valve Stick-Slip and Dead Band

valves even though they were outfitted with digital positioners. More actuator torque does not solve the problem. The time it takes for the controller output to work through the dead band is dead time that increases the errors from load disturbances. The problem is not seen for set point changes or step changes in the controller output that are much larger than the dead band. Thus, loop analysis or tuning based on large set point changes or upon open loop step tests or relay auto tuner methods will not reveal the additional dead time [Ref. 6.1]. If you consider that the peak error and integrated error for load upsets are proportional to the dead time and dead time squared, respectively, dead band is a hidden menace [Ref. 6.4]. There is some consolation in that for pure dead band once the valve moves, it can then respond to small changes in signal in the same direction and dead band can only cause a limit cycle in a pH loop without a self-regulating response, such as batch pH control. However, Chapter 8 will show how a limit cycle, which is a sustained oscillation of nearly equal amplitude, can also be caused by a pH loop driven between flat portions of a titration curve from too much controller gain or reset action.



Dead band adds dead time to a pH loop that is large for the slow response associated with a large vessel or a flat portion of the titration curve.

The control valve that responds best to small changes is a judiciously sized sliding stem (globe) valve with a digital positioner and a correctly sized diaphragm or electric actuator and properly tightened Teflon<sup>TM</sup> packing.



It has negligible backlash dead band and a stick-slip of less than 0.1%. A pH loop rarely needs the capacity of a rotary valve except for reactions or for slurry reagents. If a rotary valve must be used, it is critical to avoid tight shutoff and high friction packing and use a diaphragm actuator with a short shaft and splined connections between the actuator shaft and the ball, disc, or plug stem. Make sure the ball, disc, and plug are cast with its stem; otherwise, the connection between the ball, disc, or plug and its stem is another source of backlash. If high temperature or environmental packing must be used on any type of valve, increase the actuator size and positioner gain to help it better deal with the increased packing friction [Ref. 6.1].



*Use sliding stem (globe) reagent valves with diaphragm or electric actuators, digital positioners, and properly tightened low friction packing.*

A variable speed pump can be a solution but the user needs to be aware of a dead band that is artificially introduced into the electronics and the minimum discharge head requirements to prevent reverse flow for varying static heads [Ref. 6.4].

Interestingly enough, valve specifications do not require that a control valve move. A response requirement should be added to the control valve specification that details the stick-slip, dead band, and the response time for a small step in the throttle range [Ref. 6.5]. Ideally, a ramp at the expected rate of change of the loop should be used rather than a step, to reveal the dead time from dead band and the stair case from stick-slip [Ref. 6.6].

The flow through a pH control valve is much lower than through most other control valves, particularly for the last stage of a neutralization system. It corresponds to the last few drops added in lab titration. Extremely low reagent flows create a whole series of additional problems.

Small valves are more prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging. Here size does matter because most of these problems originate from extremely small Reynolds Numbers, clearances, and stem diameters [Ref. 6.1].



**The extremely small reagent valves used in pH control are prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging.**





*Use control valves designed for small flows and industrial service with rugged shafts, tight machining tolerances, and minimum stick-slip.*



*Use sizing programs that properly deal with laminar flow and offer an installed characteristic for your piping system and operating conditions.*

If there is a tendency for plugging, pulse width modulation can be used if there is a sufficiently back mixed volume to attenuate the pulses per Equation 5-3j in Chapter 5. It can also provide a linear flow characteristic and a flow large enough to be turbulent. The ratio of maximum to minimum pulse width establishes the rangeability. The maximum pulse width, and hence cycle time, determines the degree of variability that needs to be filtered and the additional dead time from the pulse off time. Now stroking time can be an issue because it is desirable to have the minimum pulse be as short as possible [Ref. 6.1]. A globe control valve that is pulsed must be rugged enough to withstand the repeated hammering of the valve seat by the valve plug. A  $\frac{1}{4}$ - or  $\frac{1}{2}$ -inch piston-actuated ball valve is usually less expensive to replace and more able to withstand on-off service than a globe control valve. Thus, a more practical arrangement for pulse width control is to pulse a small ball valve downstream of a globe control valve that is positioned to set the pulse amplitude. Even so, the life of the pulsed ball valve may not exceed six months. An installed spare ball valve in a parallel pipeline should be provided to minimize downtime.



*To prevent plugging and a transition to laminar flow for pH control on a well-mixed volume, use pulse width modulation of a fast cheap valve.*

Reagent control valves should be installed in the piping so that flow pushes up on the plug to help open the valve ("flow to open"). This avoids the vortex and instability of flow at low lifts called the "bathtub stopper effect" associated with "flow to close" valves. Valve trims can also develop a swirling action and vortices at particular lift positions and actuators can develop an instability from inadequate spring stiffness and actuator force or improper positioner design and tuning. The flow becomes erratic and changes even though the controller is in manual. Also, the valve gain is nonreproducible and may even have local reversals (negative gains). Spool type positioners should be avoided because the spool action tends to exasperate the potential for valve dither. If erratic flow or actuator and positioner behavior is suspected, request flow lab tests at your operating conditions over the whole throttle range from the valve manufacturer.



$$S_s = 0.5 * E_r$$

(6-2d)

- where:
- A = distance of center of reagent error band on abscissa from origin
  - B = width of reagent error band on abscissa
  - E<sub>r</sub> = allowable reagent error (%)
  - F<sub>rmax</sub> = maximum reagent valve capacity (kg per minute)
  - F<sub>imax</sub> = maximum influent flow (kg per minute)
  - S<sub>s</sub> = allowable stick-slip (resolution limit) (%)

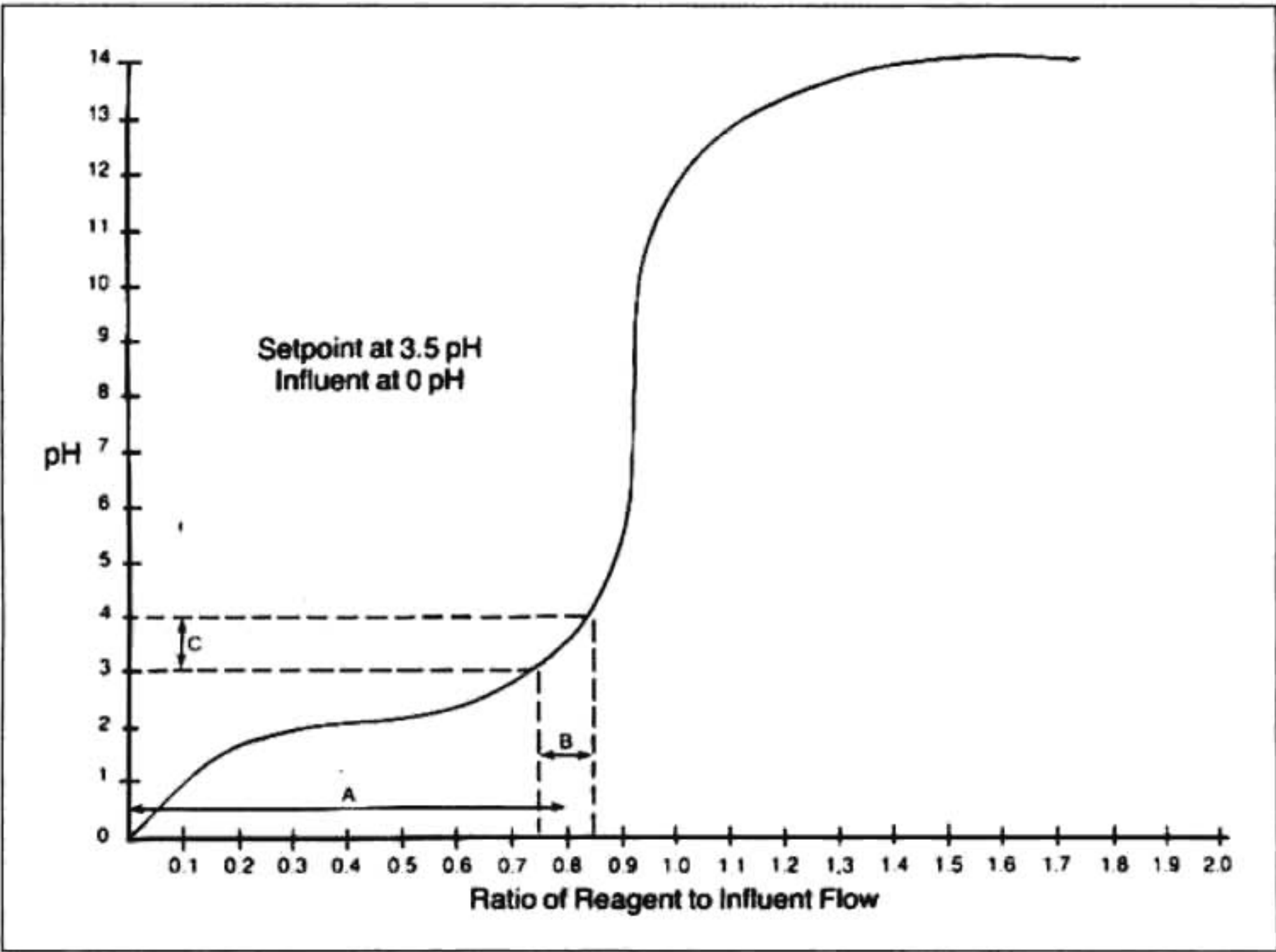


Figure 6-2a. Larger Allowable Reagent Error on a Flatter Portion of the Titration Curve

The number and type of stages of neutralization required is driven by the need to minimize the “A” parameter of the final stage and keep “B” parameter small and fast from upstream stages so that it is effectively filtered out by the volume of the final stage or intermediate volumes. For a set point near the neutral point, this leads to the classical rule of thumb (Chapter 1) from the 1960s that requires one vertical well-mixed vessel with pH control for each 2 pH units the influent is from the set point. An update to this rule takes credit for feedforward control and more precise control valves as detailed in Chapter 8. The “B” parameter from the first stage should be substituted as the input amplitude in Equation 5-3j to estimate the effect of the filtering of the volume of the next stage. Inspecting the relationships espoused in this equation reveals the first

characteristic does not exceed some specified limits. It is advisable to include the words "controllable" and "installed" because the allowable limits should be based on the magnitude of the change in slope (the valve gain) seen by the controller, and because valve stroke precision near the closed position places a practical limit on the minimum controllable flow coefficient. While the flow coefficient of some valves becomes irregular below 5% opening, the change in slope is still usually less than the change in slope over the whole stroke for an equal percentage trim, a modified parabolic trim, or a varying pressure drop. Up to now, the emphasis has been on trying to define specified limits on the inherent flow characteristic and the effect of stroke stick-slip on rangeability has been ignored in the literature. If stick-slip (which generally increases near the closed position) is ignored, the linear inherent flow characteristic yields the best, and the equal percentage inherent flow characteristic the worst inherent rangeability. However, if the effect of stick-slip is included, the opposite is true. The equal percentage inherent flow characteristic gives a 50:1 inherent rangeability for a wide range of valve stroke resolution capability because of the flatness of the characteristic curve near the closed position. Most field instrument maintenance personnel have felt that equal percentage trim gave them the greatest rangeability despite what is in the literature. Also, for static mixers, the equal percentage trim characteristic whose flow coefficient is proportional to flow helps compensate for a process gain that is inversely proportional to flow. For the well mixed tank, a linear installed characteristic is desirable if the pH controller is directly manipulating a reagent valve because the inverse relationship of process gain to flow is cancelled out by an equipment time constant that is proportional to the residence time per equations in Chapters 5 and 8. However, most pH loops on well mixed tanks now manipulate a reagent flow controller set point because of the improvement in flowmeters, which isolates the nonlinearity of the control valve from the pH controller [Ref. 6.5].



**Most statements in the literature as to valve rangeability are erroneous because they ignore the installed valve gain and stick-slip.**



***Use sliding stem valve with a digital positioner with equal percent characteristics and minimal seating friction for maximum rangeability.***

If the pressure drop available to a pH control valve decreases as the reagent flow increases because the frictional pressure drop in the rest of the system increases, a linear trim distorts toward a quick open installed





*Use a split range gap that is about twice the stick-slip or the potential error in the positioner calibration, whichever is largest.*

Normally, 50% controller output is used as the transition point for split ranging an acid or base valve. While this point is easy to remember for maintenance and operations, a better transition point for loop performance is one that equalizes the control valve gain seen by the controller over the whole signal range. The ratio of the portions of the signal range allocated for the acid and base should be equal to the ratio of the product of reagent valve capacity and reagent normality for the acid and base, as shown by Equation 6-4a. The same type of relationship holds for split ranging different or identical normality acids or bases (the normalities cancel out when equal). For example, the split range point with a 1% gap for a large linear trim valve whose capacity is 10 times that of a small linear trim valve on the same reagent should be at 9%. The small valve would stroke from 0 to 9% and the large valve would stroke from 10 to 100% of the signal.



*Choose a split range point so that the same percent change in controller output to either valve will cause about the same change in pH.*

$$S_1 = S_2 * \frac{N_1}{N_2} * \frac{F_{1\max}}{F_{2\min}} \quad (6-4a)$$

$$S_2 = 100 - G - S_1 \quad (6-4b)$$

If  $S_2$  per 6-4b is substituted into 6-4a with  $G=1\%$ ,  $X_1 = N_1 * F_{1\max}$ , and  $X_2 = N_2 * F_{2\max}$ :

$$S_1 = 99 * \frac{X_1}{X_1 + X_2} \quad (6-4c)$$

where

$F_{1\max}$  = maximum valve capacity of reagent 1 (kg per minute)

$F_{2\max}$  = maximum valve capacity of reagent 2 (kg per minute)

$G$  = gap at the split range point (%)

$N_1$  = normality of reagent 1

$N_2$  = normality of reagent 2

$S_1$  = portion of split ranged controller output allocated to reagent 1 (%)

$S_2$  = portion of split ranged controller output allocated to reagent 2 (%)

If acid and base valves are split ranged, each has an opposite effect on the pH. Since only a single pH control action can be used, one of the valve actions has to be the reverse of the other. If the two reagent valves have the same failure modes, and thus the same valve actions, the signal must be reversed for one of the valves. For a reverse pH control action, the acid valve signal should be reversed and for a direct pH control action, the base valve signal should be reversed if the control valves are both fail closed (increase to open). The opposite assignment should be used if the control valves are both fail open (increase to close). Some valve positioners and current to pneumatic (I/P) transducers have options for split ranging and signal reversing, but for accuracy, flexibility, visibility and maintainability, this is best handled by the Fieldbus functional blocks.



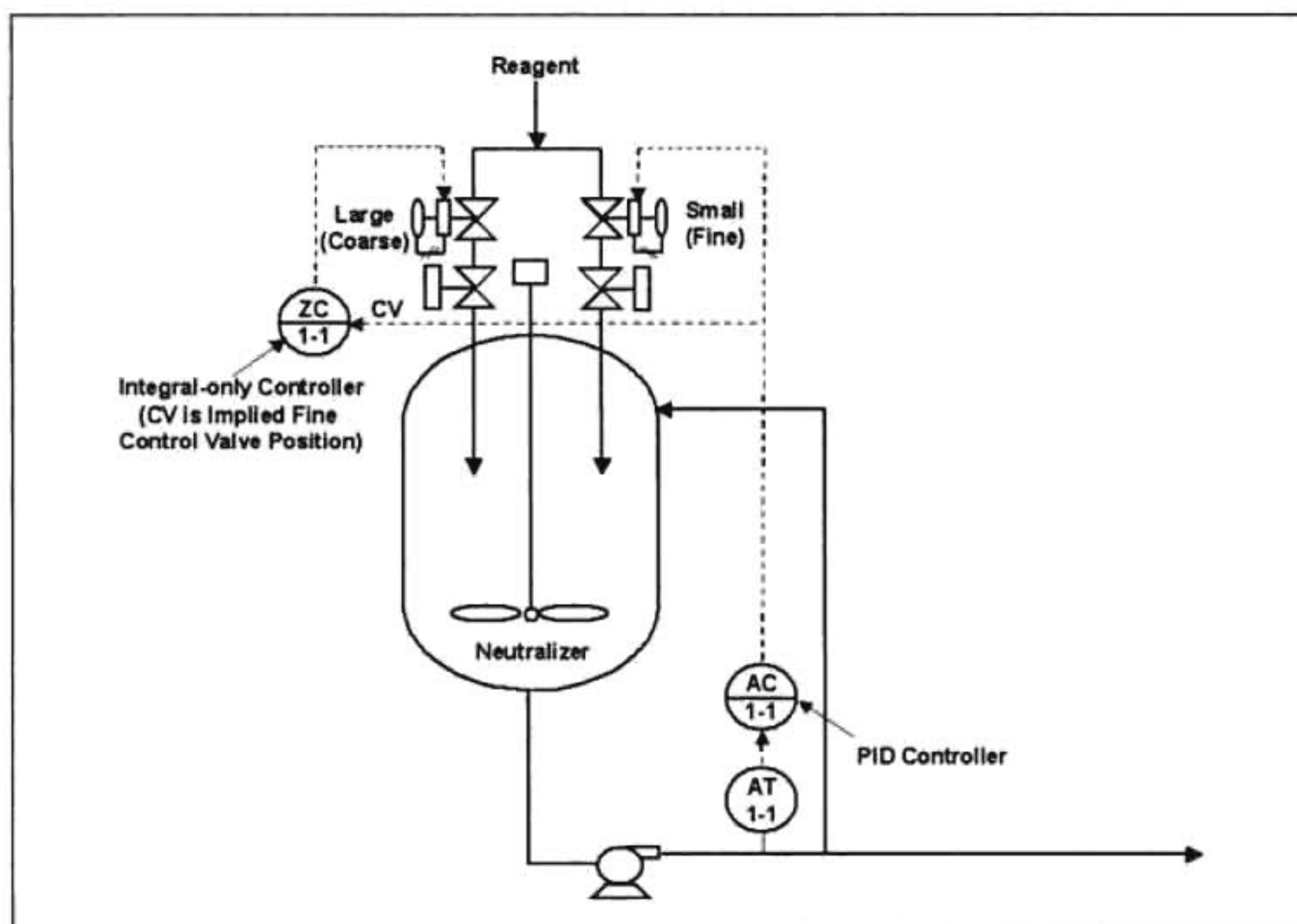
*Split ranging and signal reversing is better implemented in a Fieldbus function block than via a special calibration of an I/P or positioner.*

Various computations have been developed for split ranging equal percentage characteristic valves. While the nonlinear gain can for some specific set of influent flow and concentration conditions partially compensate for the nonlinearity of the titration curve, the assumption that these conditions always exist is tenuous. The use of reset action in a pH controller means that there is no one-to-one relationship between the measurement signal and the control valve signal. The pH controller will drive its output to whatever value is necessary to reduce the error. Thus, nonlinearity in the process or controlled variable cannot generally be compensated by control valve trim nonlinearity for proportional-integral (PI) or proportional-integral-derivative (PID) controllers.

## 6-5. Special Strategies

A small reagent control valve for fine adjustment in parallel with a large control valve for coarse adjustment meet the resolution and rangeability requirements but the two valves will fight. To reduce this interaction problem, the output of a separate proportional-only controller can be used to position the small valve, as shown in Figure 6-5a, or the output of a valve position controller can be used to position the big valve, as shown in Figure 6-5b. The measurement for the valve position controller is small valve position and the set point is 50%. The valve position controller has the advantage of ensuring that the small valve precision is always available by keeping it near the middle of its stroke range by slowly adjusting the big valve. Since the valve position controller uses slow integral-only action to reduce interaction between it and the pH controller, this configuration is sluggish for large load changes. Feedforward control should be implemented to position the coarse valve for large feed upsets





**Figure 6-5b. Integral-Only Valve Position Control of a Coarse Adjustment Valve to Reduce Interaction with Fine Adjustment Valve**


noise problems for inline pH control systems. Also, since the metering pump is normally located at grade level and is not close-coupled to a pipe or vessel nozzle, the reagent delivery delays can be enormous if the reagent drains back through the pump or into the vessel or the process fluid back fills into reagent delivery system.



**Metering pumps tend to have limited inherent or self-imposed rangeability and exhibit noise from pulsing and huge reagent delivery delays.**

Lime feeders have a transportation delay that is proportional to the length of the feeder divided by its speed. This transportation delay may be several minutes. The residence time of a vertical tank must be at least 20 times as large as the sum of this delay, lime dissolution time, and turnover time for the vessel to be classified as well-mixed. To eliminate the need to increase the vessel size, and correspondingly the agitation power, the lime rotary valve speed can be base loaded and the pH controller can manipulate the conveyor speed or the influent flow. If the pH controller manipulates the waste flow, the dissolution time associated with an increase in lime delivery rate is also eliminated. The level controller on the

influent tank slowly corrects the lime rotary valve base speed if the waste inventory gets too high or low. A notch gain or error squared level controller or MPC is used to suppress control action when the level is in mid-range. A 50% output from the level controller corresponds to a zero correction of the base loaded rotary valve speed. The operator can change the system capacity by changing the speed through a manual loader. Figure 6-5c shows this method of eliminating the reagent transportation delay and dissolution time of the lime by the manipulation of waste flow to control pH.

 *To eliminate the transportation time delay and dissolution time associated with a lime feeder system, manipulate the waste flow for pH control.*

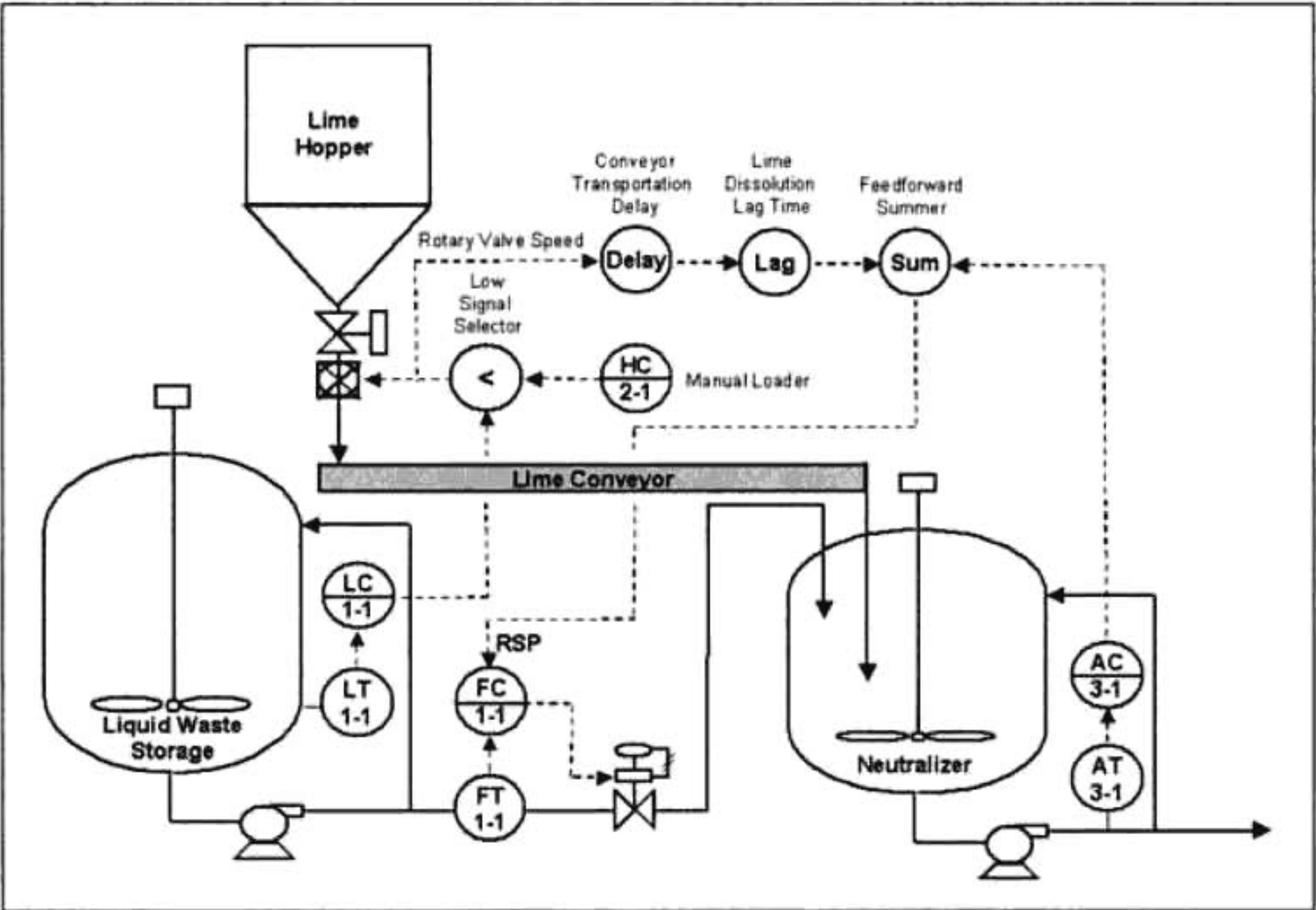


Figure 6-5c. Throttling of Waste Stream to Eliminate Lime Feed Transportation Delay and Dissolution Time for pH Control



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# **Chapter 7: Reagent**



## Chapter 7

### Reagent

#### 7-1. Delivery Dilemmas

For good pH control, a small change in reagent dosage needs to be delivered precisely, reliably, and quickly into the middle of a mixture. This becomes an exceptional challenge for the extremely small flow required for most pH control systems and translates into specific demanding requirements for reagent selection and piping design.

For a reagent dose to be precise enough, the reagent's logarithmic acid dissociation constant ( $pK_a$ ) should be close to the pH set point so that it tends to flatten the titration curve reducing the effect of valve stick-slip. weak acids, such as acetic acid, and weak bases, such as ammonia, have a  $pK_a$  close enough to 7 pH to reduce the precision requirement and possibly the number of stages of neutralization. The reagent viscosity should also be low enough to insure fully turbulent flow important for consistent dosing. For the delivery to be reliable, the reagent should be free from solids and slime because of the tiny control valve trims used. For a reagent delivery to be fast requires that the reagent viscosity be low enough for the dose to start quickly and mix rapidly with the effluent. An extraordinary time delay has been observed for starting the flow of 98% sulfuric acid through an injection orifice because of its high viscosity. It has been compared to getting ketchup out of a bottle [Ref. 7.1]. The mixing of a viscous stream, such as 98% sulfuric acid or 50% sodium hydroxide that is about 40 times more viscous than the typical effluent stream, is difficult and requires greater agitation intensity and velocity. For static mixers it means more mixing elements and higher pressure drops. A highly viscous reagent dose tends to travel as a glob through the mixture. Lastly, the reagent should be in the liquid phase.

The neutralization reaction of liquid components is essentially instantaneous once mixed. Gas or solid reagents take seconds and minutes, respectively, to dissolve and get to the point of liquid contact of the components. Reagent bubbles escape as a vapor flow when the bubble break up time and gas dissolution time exceeds the bubble rise time. Reagent particles travel downstream and accumulate on the walls of piping and equipment and pump strainers when the solid dissolution time exceeds the shortest residence time. Unreacted ammonia and calcium hydroxide (lime) reagent have been the source of huge and largely undocumented extra reagent and additional emissions and solids disposal costs. Coating and plugging of upstream control valves and downstream from particles of unreacted reagent or from precipitation of salts from



reacted reagents can be so severe as to cause excessive equipment maintenance and downtime. Liquid reagents, such as ammonia, that can flash in the vena contracta of a control valve can choke the valve or cause cavitation damage in the valve and the piping immediately downstream. Particles in the reagent can cause erosion of control valve trim. Some waste lime systems have rocks that can quickly tear up a valve seat and plug [Ref. 7.1].



*To help ensure a precise, reliable, and quick reagent delivery, use low viscosity liquid weak acid and weak bases that contain no bubbles, particles, rocks, or slime and cause no excessive precipitation of salts.*



**Gaseous and solid reagents often have huge hidden costs from additional reagent consumption, emission, solids disposal, and maintenance costs.**

If the reagent pipeline is partially filled or empty or a dip tube or injection tube is back filled with process fluid, the reagent delivery delay becomes the biggest source of dead time in a pH loop for the small reagent flows commonly required for neutralization. Whenever a reagent control valve closes or a metering pump stops, reagent continues to drain into the process and process fluid can be forced back up into the reagent injection or dip tube. Even if hydraulics don't promote much drainage or back filling of the tubes, the migration of ions from high to low concentrations will proceed until an equilibrium is reached between the concentrations in the reagent tube and the process volume. As a result, the pH will continue to be driven by a drainage and migration of reagent after the control valve closes or the metering pump stops. If the valve is closed or the pump is stopped for a long time, when the valve opens or the pump starts, it must flush out process components in the tubes before the reagent gets into the volume. The worse case delivery time delay is the volume of the backfilled tube divided by the reagent flow. Since dip tubes are designed to be large enough to withstand agitation and the design standard for normal flows is to take the dip tube down toward the impeller, the reagent delivery delay can be several orders of magnitude larger than the turnover time described in Chapter 6. For example, if the reagent flow is 1 gallon per hour and the submerged reagent dip tube volume is 2 gallons, it would take 2 hours for the reagent to get into the vessel, which is almost 1000 times larger than the dead time from the turnover time in a well mixed vessel. While this is an extreme case that usually only occurs during start-up or batch operations, it is symptomatic of the reagent piping being a big potential source of dead time that is often overlooked during reagent delivery system design [Ref. 7.1].



When a section of reagent pipeline is empty because of drainage and a siphoning effect, the time delay to fill the pipe is the volume of the empty pipe divided by the reagent flow.

If there is insufficient back pressure to keep the pipeline full, then the delay is the time for a wave of process fluid to propagate down the horizontal sections and to dribble down the vertical sections. If reagents are mixed or diluted inline, the time delay is the piping volume from the mixing point to the entry point divided by the combined flow.



**The delivery delay from an empty or backfilled reagent pipe, injection tube, and dip tube is the largest source of dead time in a pH loop.**

The best case is when the reagent piping and tubes are completely filled with a non-compressible liquid reagent of constant concentration. A change in valve position causes a pressure wave to travel at the speed of sound in the fluid from the valve that upon arrival at the entry point into the process initiates a change in reagent flow within a second or two. check valves can be used on the tip of injection and dip tubes to achieve this condition if they can be designed reliable enough for the process service and a reagent flowmeter is installed to verify reagent flow. Since the check valve is difficult to replace and its integrity is suspect, it is not a popular solution. An automated on-off isolation valve close-coupled to the process connection that closes when the control valve throttle position is below a reasonable minimum helps keep reagent lines pressurized and full of reagent. For metering pumps, an isolation valve should be added to the pump suction to prevent the reagent from draining back through the pump [Ref. 7.1].



**If the complete reagent delivery system can be kept pressurized with a constant liquid reagent composition, the delivery delay is negligible.**



***Add an automated isolation valve close-coupled to the process connection and in the suction of a metering pump that closes when the control valve closes to prevent the draining and backfilling of reagent piping.***

The distance between the reagent control valve and the process connection should be minimized even in the case where there is an isolation valve to minimize the transportation delay of changes in reagent concentration and



the amount of reagent trapped between the valves. To protect against over pressurization from thermal expansion in a trapped section, a relief valve is installed with its discharge piped to a reagent storage or collection vessel.

The best method of reducing reagent delivery delay and mixing dead time is to inject the reagent flow into a feed or a recirculation line. The high feed or recirculation flow provides premixing, minimizes transportation delay for a properly selected injection point, and creates a better dispersion of the reagent at the entry point into the process. It enables the use of conventional dip tube design. However, localized high concentrations of reagent acids and bases may necessitate pH control and/or special materials of construction between the injection point and entry point into the volume. If the pH is controlled in a feed line and recirculation line, the injection point is normally into a static mixer and pump suction, respectively. If reagent addition is manipulated by a loop to control the pH in a vessel rather than in a pipeline, the injection point should be within 20 pipe diameters of the entry point into the vessel. A static mixer can improve the premixing, although the reduction in pH noise may not be noticeable for a large vessel.



*The best method of reducing reagent delivery delay and mixing dead time is to inject the reagent into a high feed or recirculation flow.*

## 7-2. Dilution

A common misconception is that the slope of the titration curve, and hence the sensitivity of the system, can be decreased by reagent dilution. Reagent dilution has a negligible effect on the shape of the titration curve: the curve slope will appear larger if the same abscissa is used because only a portion of the original curve is displayed. The numbers along the abscissa must be multiplied by the ratio of the old to new reagent concentration to show the entire original titration curve. For example, the abscissa values would have to be doubled if the concentration of the reagent were cut in half. While the allowable reagent error band is increased, the reagent control valve capacity requirement is also increased by the same factor so that the valve resolution requirement does not change.

Properly designed dilution systems offer a variety of performance benefits. Most chemists will use diluted reagents to make a titration easier and more accurate. Since this is true for the lab, you can imagine how much more important it is in the field fraught with less-than-ideal conditions. Dilution can reduce reagent valve plugging, reagent transportation delay, and reagent viscosity. It can prevent laminar flow



and partially filled pipes, and dramatically improve dispersion in a mixture. It also decreases the freezing point and winterization problem and corrosion for sodium hydroxide.



**While the shape of the titration curve doesn't change much by dilution, dilution can dramatically decrease reagent delivery delays, improve reagent addition reproducibility by eliminating transitions to laminar flow, increase valve reliability by reducing plugging, and enhance mixing by increasing the reagent injection velocity and reducing the differences in viscosity and density between the reagent and the influent, which is normally a dilute water stream.**

If reagent dilution is used, the system must be carefully designed to prevent the creation of reagent concentration upsets and reagent delivery delays. The pH controller should throttle the diluted reagent. The mass flow of water should be ratioed to a mass flow of reagent and a density controller should trim the ratio. Coriolis flowmeters should be used to improve the mass flow measurement reproducibility and provide an accurate density measurement for concentration control as shown in Figure 7-2a. Additionally, one could utilize the temperature from the coriolis meter to compensate the density, particularly if the feed temperature is not constant. If the pH controller throttles the undiluted reagent or the water, the reagent delivery time delay is for the plug flow concentration response instead of for a liquid flow response. The time delay for the concentration response is approximately equal to the residence time whereas the time delay for a full pipeline liquid flow response is less than 1 second. If the titration curve is steep, the fast concentration disturbances from flow measurement inaccuracy and noise may cause pH excursions outside of the control band. For example, the single step neutralization of 0 pH hydrochloric acid with sodium hydroxide would require a flow measurement accuracy of 0.0001 % for reagent dilution to achieve a 2 pH control band about a 7 pH set point. If a static mixer is used for pH control, the fast concentration disturbances from reagent dilution will create pH measurement noise. Therefore, for steep titration curves and inline pH control, a storage tank for diluted reagent should be installed to smooth out the fast reagent concentration disturbances from dilution.



***Use Coriolis mass flowmeters to provide mass flow ratio control of water to reagent corrected by a Coriolis density loop that feeds a diluted reagent vessel volume sized to smooth out concentration fluctuations to the pH loop.***







## 7-4. Dissolution

Dissolution is the act of dissolving. Whereas the pH reaction time rarely exceeds a few seconds, the dissolution time of some solid or gaseous reagents can be several minutes. The dissolution time is equivalent to the batch conversion time and can be found by adding a shot of reagent to an influent sample in a beaker and noting the time between the shot of the reagent and 99% conversion. The beaker must have the same degree of agitation as the field vessel. A pH measurement can be used to note the 99% conversion point but a steep titration curve slope will probably result in a shorter than actual dissolution time measurement and a flat titration curve will probably result in a longer than actual dissolution time measurement. If the reagent is continuously added instead of pulsed, the pH measurement may suddenly approach the final value and then rapidly return back to the previous value due to dynamic changes in solution saturation. These "rebounds" add ambiguity to the time measurement.

A back-mixed vessel is much better than a plug flow vessel for control because it has a much lower dead time to time constant ratio. However, the residence time distribution has a much greater spread. Some of the material is in the vessel for a time much smaller than the residence time for continuous operation. Consequently, a greater residence time is required for a continuous back-mixed vessel for conversion of lime. The plot in Figure 7-4a shows that the residence time of a continuous back-mixed vessel must be 20 times the dissolution time for 99% conversion [Ref. 7.2]. The agitator pumping rate must be scaled up in proportion to the vessel volume so that the equipment dead time to time ratio remains the same. Since the horsepower required is proportional to the third power of the pumping rate, the additional energy cost may be greater than the savings from using lime instead of caustic as a reagent. The capital cost of the larger vessel and motor may also be significant. If the size of a single back-mixed vessel becomes prohibitive, several smaller ones in series can be used to achieve the desired conversion percentage. The effect of these vessels in series on conversion is multiplicative in terms of conversion fractions as shown by Equation 7-4a. For example, two vessels, each with a residence time that is twice the dissolution time will have an individual conversion of 90% and an overall conversion of 99%.

$$X_o = X_1 * (1 - X_1) * X_2 \quad (7-4a)$$

where:

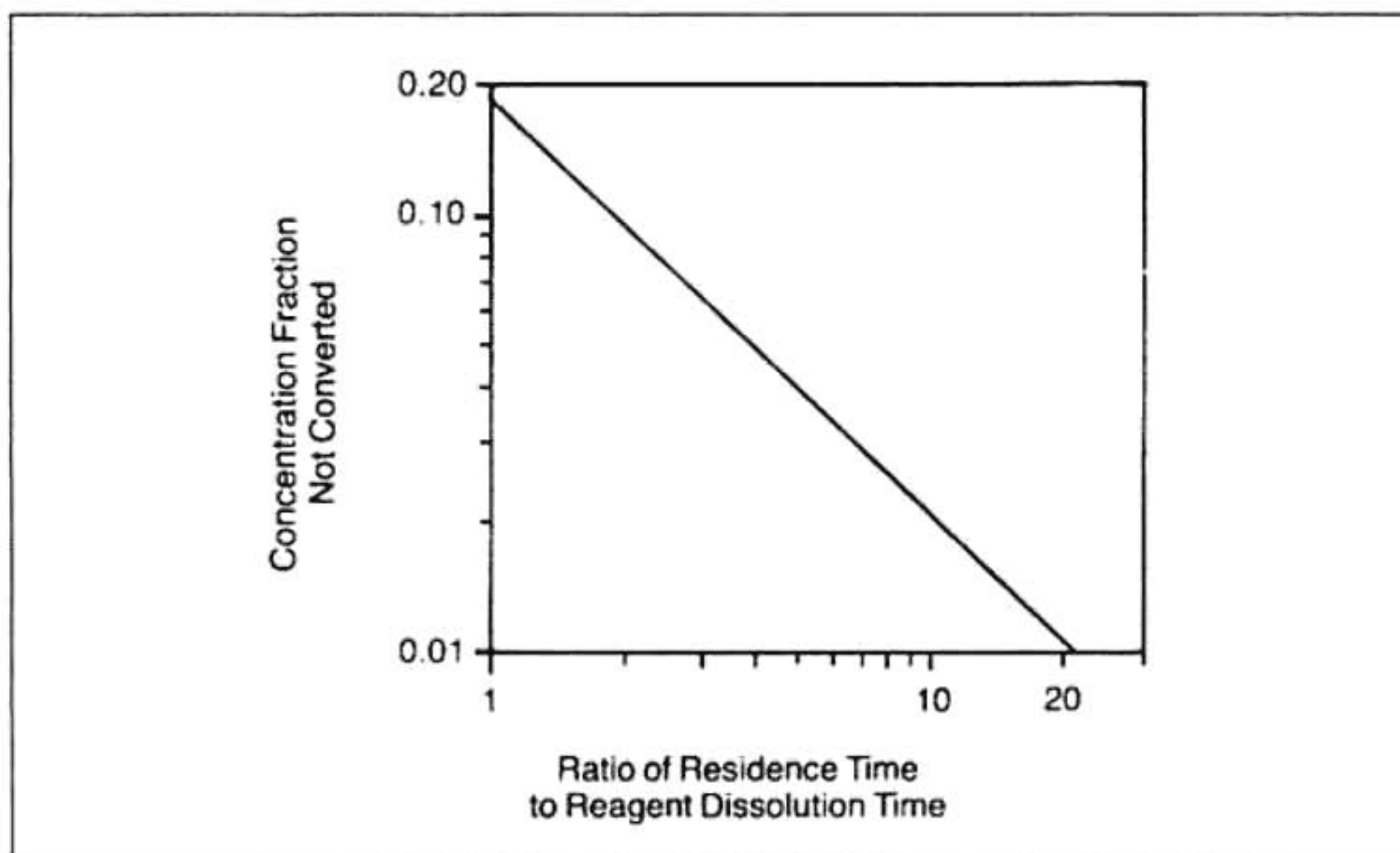
$X_o$  = overall conversion fraction at the outlet of the last vessel

$X_1$  = conversion fraction at the outlet of the first vessel

$X_o$  = conversion fraction at the outlet of the second vessel



*For multiple stages, use lime on the first stage rather than on the last stage to decrease the amount of unconverted lime downstream.*



**Figure 7-4a. Concentration Fraction of Lime not Converted in a Back-Mixed Vessel**

The dissolution time has an effect on a control loop similar to a slow reagent control valve because the change in the quantity of dissolved reagent lags the change in the pH controller output. The equivalent slow valve time constant is approximately equal to one-fifth the dissolution time. Most of this time constant is converted to loop dead time that increases the ultimate period of the pH loop on a vessel. Chapter 8 will quantitatively show the effect of this time constant on the ultimate period and the controller mode settings. If the influent flow can be throttled, it is best to eliminate the slow manipulated variable by base loading the lime feed rate and throttling the waste influent flow for pH control in the fashion illustrated in Figure 6-5c for lime feeders.

The dissolution time of limestone is too large to allow its use for feedback control, even when pulverized into fine particles. The main use of limestone is for manual treatment of acid spills by covering the spill area or diverting the spill to a limestone pit. The dissolution time of pulverized dry lime can be greatly reduced by slaking the lime and making it into a lime slurry. Figure 7-4b shows that the dissolution time for pulverized dry lime is about 32 minutes and the dissolution time for lime slurry is about 8 minutes when added to a 1000 milliliter sample of wastewater in a 1500 milliliter baffled beaker with a 100 rpm three blade agitator. The above data is for "soft burned" lime. If the lime is heated in the kiln longer, the



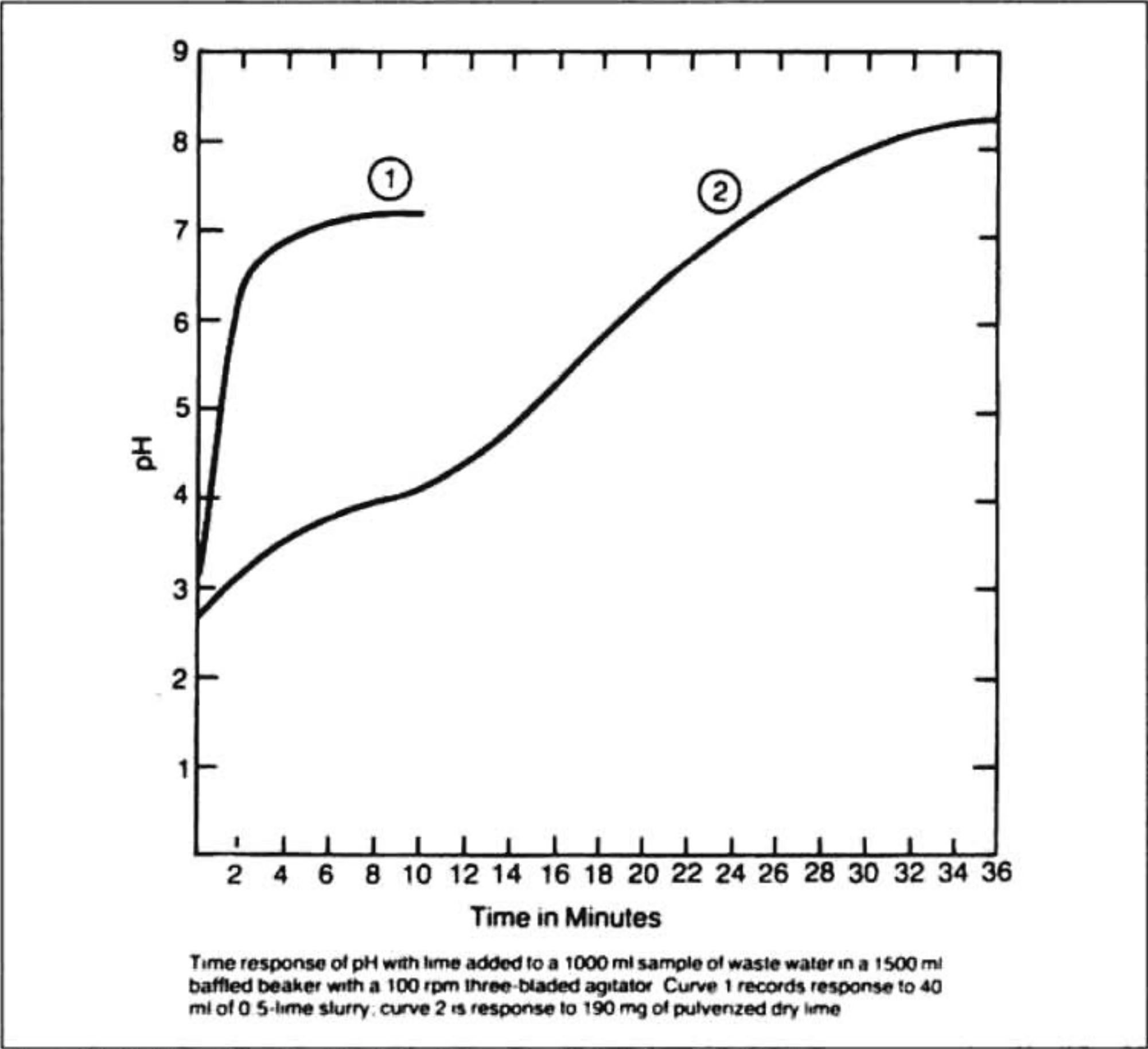


Figure 7-4b. Time Required for Lime Slurry and Dry Lime to Dissolve

lime becomes “over burned” or “head burned” and takes a longer time to dissolve. dry lime tends to lay on the surface unless wetted and forced below the surface by a water spray. Therefore a water spray should be used for dry lime addition. The dissolution time of lime slurry increases with age due to the agglomeration of small particles into larger particles even though the lime slurry storage tank is mildly agitated [Ref. 7.3]. If the pH controller manipulates the lime feeder or water addition to the lime slurry storage tank, the equipment time constant of the slurry tank has the same effect as a slow valve time constant. To prevent the addition of this time constant to the loop, a slurry tank level controller should manipulate the lime feeder speed, and the water addition rate should be ratioed to the lime feeder speed. The pH controller should manipulate the lime slurry addition to the neutralization vessel. The lime slurry feed must be kept flowing by using a recycle loop to prevent settling and plugging of the reagent lines. A throttled globe control valve will plug. The liner of a pinch diaphragm valve will fail due to erosion. pulse width modulation of an on-off ball valve is the best alternative because it has the least

## Chapter 8

### Control System

#### 8-1. Feedback Control

Nearly all control loops utilize some form of feedback control. The most prevalent type of controller is a proportional-integral (PI). A PI basically provides a controller output that is the sum of a contribution that is proportional to the pH error and the integral of the pH error, where the error is the difference between the pH set point and the measurement. If the pH loop is on a vessel where there is a large time constant that provides a smooth transition in pH, it is beneficial to include rate action to form a proportional-integral-derivative (PID) controller so that there is a contribution to the controller output that is proportional to the rate of change of the pH or the control error. If the set point is on a flat part or a bend in the curve, rate is particularly effective at dealing with the drastic acceleration associated with an excursion to the steep portion of the curve.

Rate action on the measurement instead of the error is preferred to eliminate bumps to the controller output from step set point changes by the operator. However, for set point changes by model predictive or supervisory control and a batch sequence, rate action on error will help the controller recognize that the set point change is intended.

The loop block diagram in Figure 8-1a details the dynamics that determine the PI and PID controller tuning settings and the loop's performance. The reagent flow starts to correct for a disturbance, such as a change in influent composition or flow, only after it appears in the effluent, the controller sees it and reacts, and the reagent flow responds and gets into the process at the same point as the disturbance. No matter where the upset enters, information must complete one cycle around the loop for a corrective action to take effect. The time delay between the start of the disturbance and the arrival of the corrective action is the total loop dead time. If the dead time was zero, the pH would stay within the resolution limit of the measurement and the control valve at the set point. Since the pH would hardly budge from its resting value on the titration curve, the variation in slope of the curve would be a mute point. While it is not possible to have a zero dead time, it is more important in pH control than in any other loop to make this dead time as small as possible to reduce the effect of the extreme process nonlinearity typical for pH applications.

The total loop dead time is the sum of the valve dead time from dead band, stick-slip, and actuator pre-stroke delay and stroking time, the reagent delivery delays, equipment mixing delay, and sensor dead time



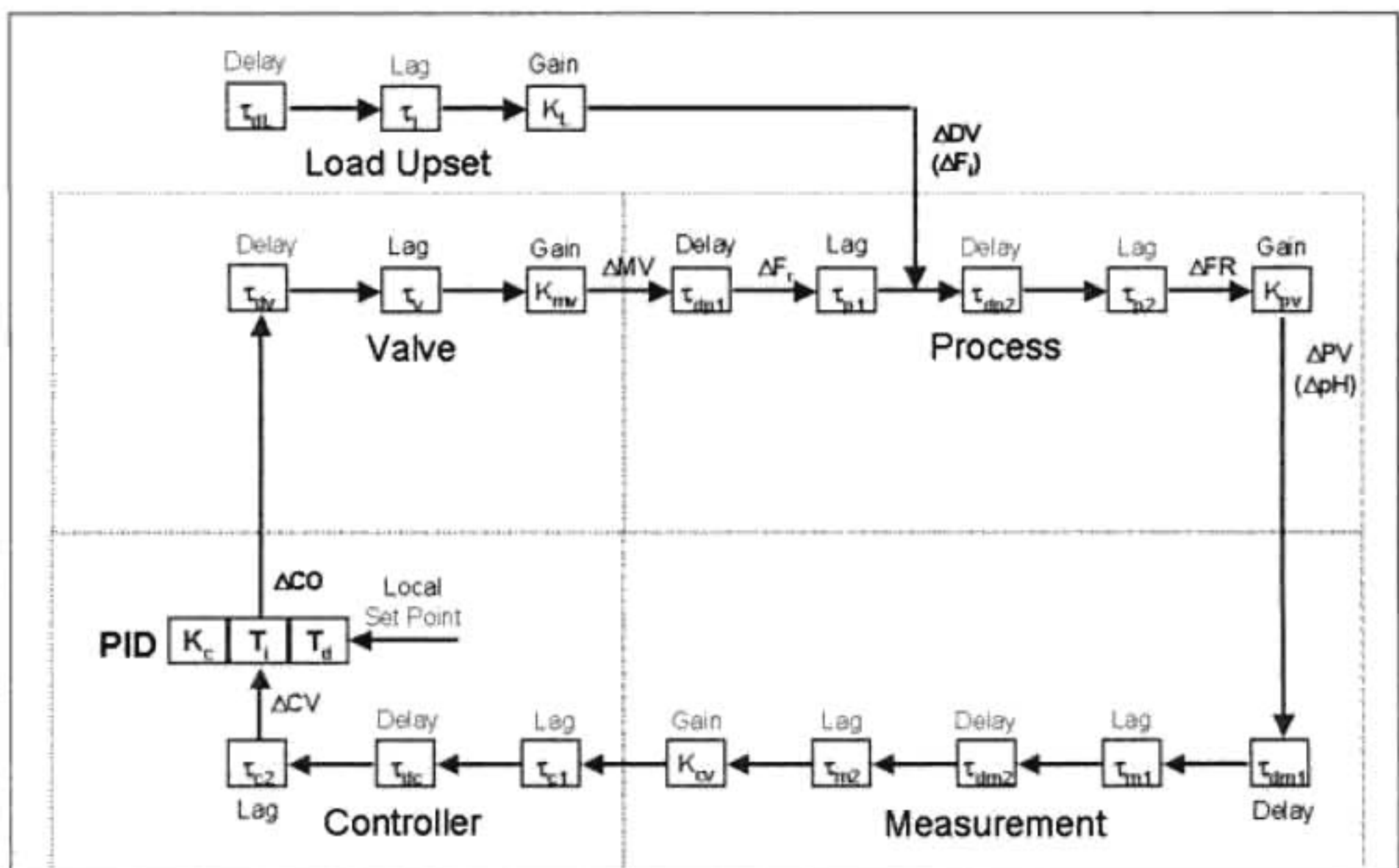


Figure 8-1a. Block Diagram for pH with the Major Sources of Dead Time Noted



More so than for any other loop, it is important to reduce dead time for pH control because it reduces the effect of the nonlinearity.

from transportation delay, sensor time constant, digital control cycle time, and filter time constants introduced into the transmitter or controller. The fraction of a small time constant that is converted to dead time will be detailed in the section on controller tuning, but for now small time constants for pH loops on a vessel can be considered to be effectively dead time since the sources of dead time are usually underestimated.



*Add up the pure time delays and the effective time delays from small time constants for one pass around the control loop to get the total dead time.*

## 8-2. Feedforward Control

Feedback control only takes action after an error has developed. The error must be large or persistent before feedback control makes a large correction for an upset. Feedforward control has the noble idea of calculating a corrective action to compensate for an upset before an error appears. The most common load upsets (disturbances) are influent feed and composition. flow feedforward is widely used and is often referred to as ratio control since the reagent flow is ratioed to the influent flow. The



ratio is the abscissa of the titration curve for the pH set point if the X axis is properly converted to a ratio per Equations 2-1g through 2-1k for pH system design.

The reagent and influent upset may enter the process equipment literally at the same point if the reagent is combined with the influent stream, otherwise they take different but hopefully similar paths. There is a series of dead times and time constants in each path as shown Figure 8-2a. The feedforward signal is typically added to the pH controller output. If the combined signal goes directly to a reagent control valve, the feedforward calculation is complicated by the nonlinearity and sizing of the control valve. The use of a good reagent flow measurement, as described in the next section for cascade control, eliminates this difficulty of computing a valve position that corresponds to a desired flow. While theoretically a feedforward multiplier instead of a summer should be used on a pH controller output that directly manipulates a linear valve for flow feedforward for a static mixer, scaling issues make this undesirable.

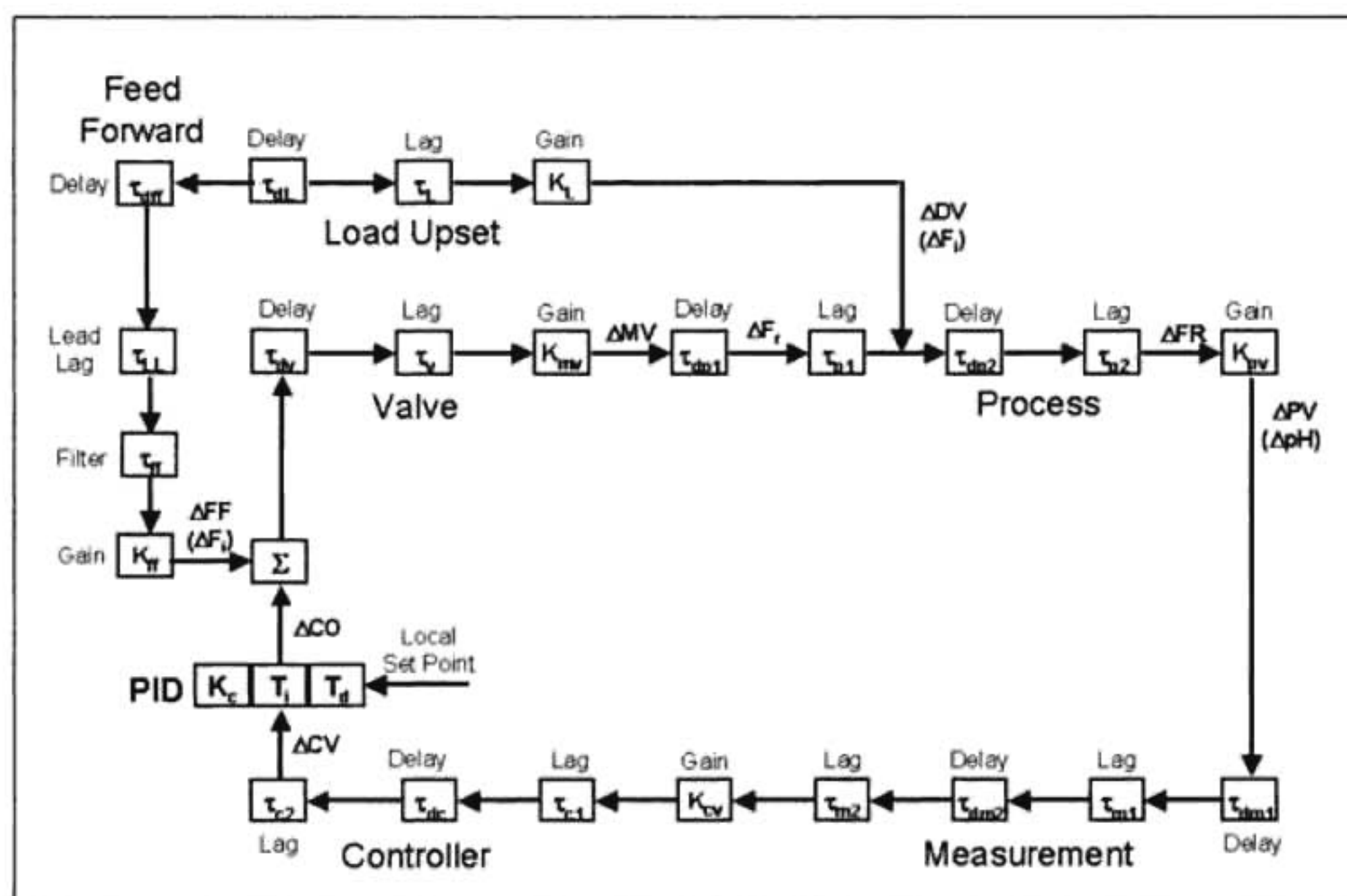


Figure 8-2a. Block Diagram of the Paths of an Upset and a Feedforward Signal

The effectiveness of feedforward control depends on the accuracy of the measurement of the upset and the calculation and timing of the corrective action. In order for there to be no error, the corrective action must arrive in the process at the same point and time as the upset with an opposite but equal value to the upset. The disturbance measurement is first filtered to eliminate noise. The timing (dynamic compensation) is then set via a lead-



lag and a dead time function block. Nearly all books and articles on feedforward control setup and tuning take a simplified view where the corrective action (reagent) and load disturbance (influent) are combined as process outputs. The feedforward lead time is set equal to the lag in the path of the corrective action (reagent) and feedforward lag time is set equal to the lag in the path of the disturbance (influent).

Since in reality the corrective action (reagent) and disturbance (influent) are process inputs, the approach commonly taken in the literature is not right and results in large settings of both the lead and lag times. An error in one of these settings can lead to a serious timing error. In particular, a larger than needed lead setting will amplify noise and cause inverse response by a feedforward signal that arrives too soon. Inverse response is where the initial direction of a change is the opposite of the final direction of the change. Needless to say, it confuses the heck out of the controller. noise and inverse response can cause a feedforward control system to do more harm than good.



**The reagent correction from feedforward must arrive at the same point and time as the influent upset with an equal but opposite equivalent value.**

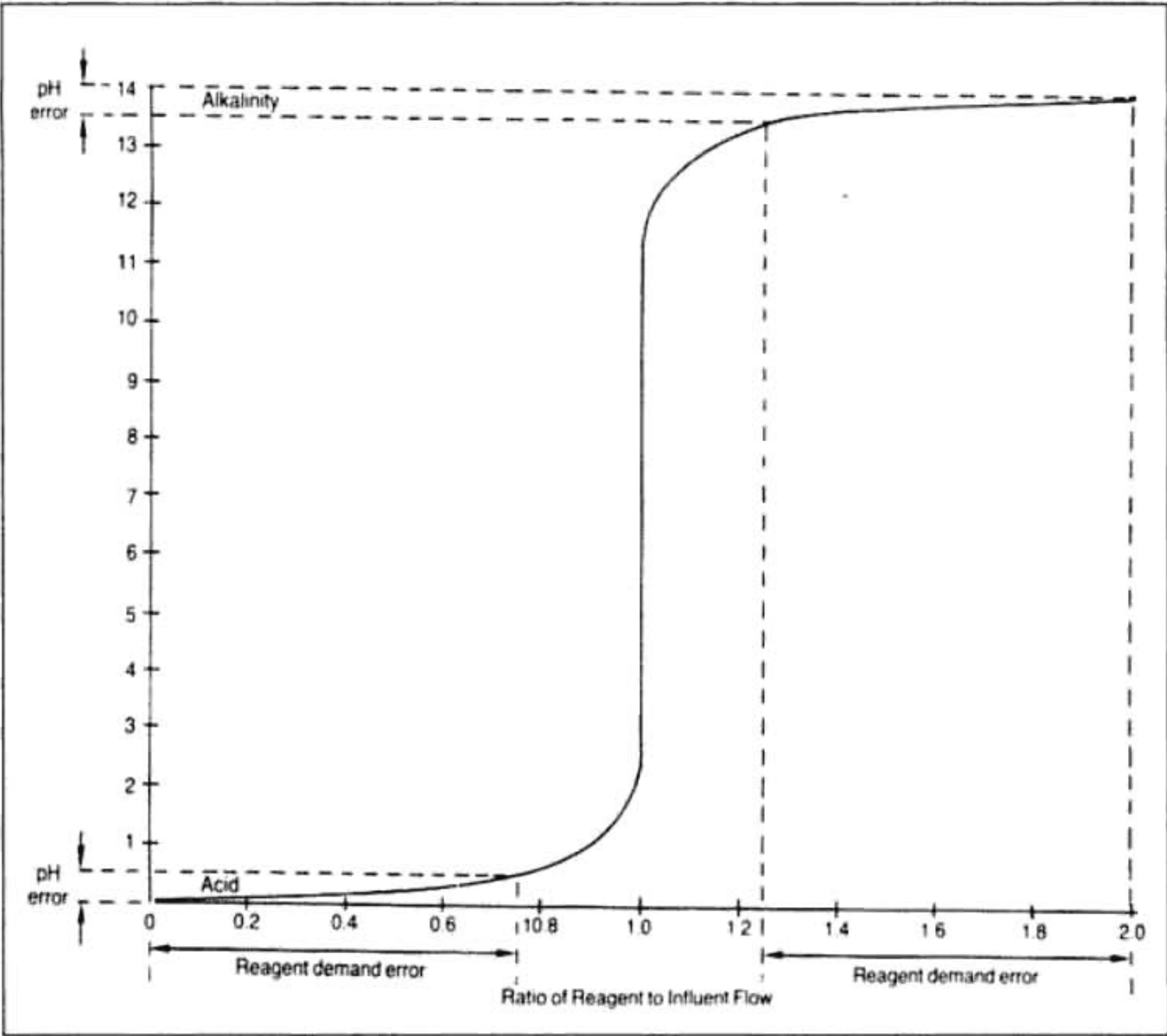


***Filter the feedforward signal to remove noise and make sure the corrective action does not arrive too soon and cause inverse response.***

The lag times in the corrective action and disturbance path are normally similar enough to warrant the exclusion of the calculation of lead and lag times. While a lead time might help kick a valve signal to get it to move, this is difficult to get right and if it is too large it creates additional slip. Besides, the stick-slip in reagent valves must be minimized because of the extreme sensitivity of pH. In some rare situations, the kicking action has helped break the trim free of solid buildup, but the burst of reagent flow causes overshoot. The one solid case where a lead would prove beneficial is in the cancellation of a lag time associated with dissolving calcium hydroxide (lime) or magnesium hydroxide particles. Here, the lead time should be set equal to the reagent lag time, which is about  $1/5$  of the dissolution time. Whenever a lead time is used, the lag time should be at least  $1/8$  the lead time to prevent the excessive amplification of noise.



***If the reagent has particles, then set the feedforward lead time equal to dissolution lag time; otherwise omit the use of a lead-lag in the feedforward.***



**Figure 8-2b. Huge Reagent Demand Error from pH Feedforward Measurement Error**

and the new controller with a remote set point is called a secondary or inner loop controller. A valve positioner, such as a digital valve controller, is a secondary controller that compensates for stick-slip and gets its remote set point from the process controller. The next most common cascade control system uses a secondary flow controller that compensates for pressure upsets and the nonlinearity of the reagent valve. There were many failures of this usually sound concept of pH to flow cascade when orifice meters were used because the flow signal became erratic and caused more harm than good for low flow and transitions to laminar flow. Improvements in the technology of inline flow meters now makes the cascade of pH to flow desirable to isolate the pH controller from changes in the valve gain and facilitate ratio control. The first, second, and third choices in terms of rangeability and insensitivity to Reynolds Number and straight pipe runs is a Coriolis, magnetic, and vortex flowmeter, respectively [Ref. 8.3]. The vortex meter is a distant third choice because of signal drop out at low flow, the sensitivity of the meter coefficient to viscosity, and straight pipe length requirements. For pH loops, there is a triple cascade where the pH controller output is the remote set point of a



reagent flow controller whose output is the remote set point of a digital valve controller (digital positioner).



*Use a Coriolis or magnetic flowmeter for reagent flow control.*

To get the most benefit from cascade control, the secondary loop dead time and time constant should be five times faster than the primary loop dead time and time constant. If this is not the case, one of the controller gains and reset time settings will need to be decreased and increased respectively, to prevent excessive cycling from interaction of the two loops. The time constants and dead times for the position of a small reagent valve and the flow in a pumped full pipeline are all less than 1 second, which on the surface violates the cascade rule where the secondary loop must be five times faster than the primary loop. However, the digital valve controller has no integral action and a scan time that is more than five times faster than the flow, and the flow controller normally has a filter time and low controller gain setting to deal with the measurement noise and valve nonlinearity. In the days of pneumatic positioners and electronic analog controllers and for large valves, the interaction problem was severe enough for a rule to be generated where boosters instead of valve positioners should be used on fast loops, such as a flow loop, based on a Nyquist plot analysis that forgot that reality reeks. This was a disastrous rule even back before the advent of digital valve and process controllers because it ignored the nasty consequences of sticking, jumping, and wandering valve plugs and discs from improper bench settings, stick-slip, and the poor inlet and the high outlet sensitivity of boosters [Ref. 8.5]. Every reagent valve must have a digital positioner (digital valve controller), no ifs, ands, or buts.



*Every reagent valve must have a digital valve controller.*

The cascade of pH to reagent flow on a static mixer also appears to violate the cascade rule because the dead time and time constant of a filtered flow loop are a couple of seconds, which is almost the same as the transportation delay through the mixer and the clean electrode time constant for a buffered system. However, the additional dead time of the reagent injection and the transportation delay from the mixer to the electrodes makes the pH loop dead time at least 6 seconds and for strong acid and base systems, the electrode time constant is at least 4 seconds and a digital pH filter time of 12 seconds is often used to screen out axial noise and enable an averaging control of sustained oscillations [Ref. 8.5]. The cascade control of mixer pH to reagent flow greatly improves the

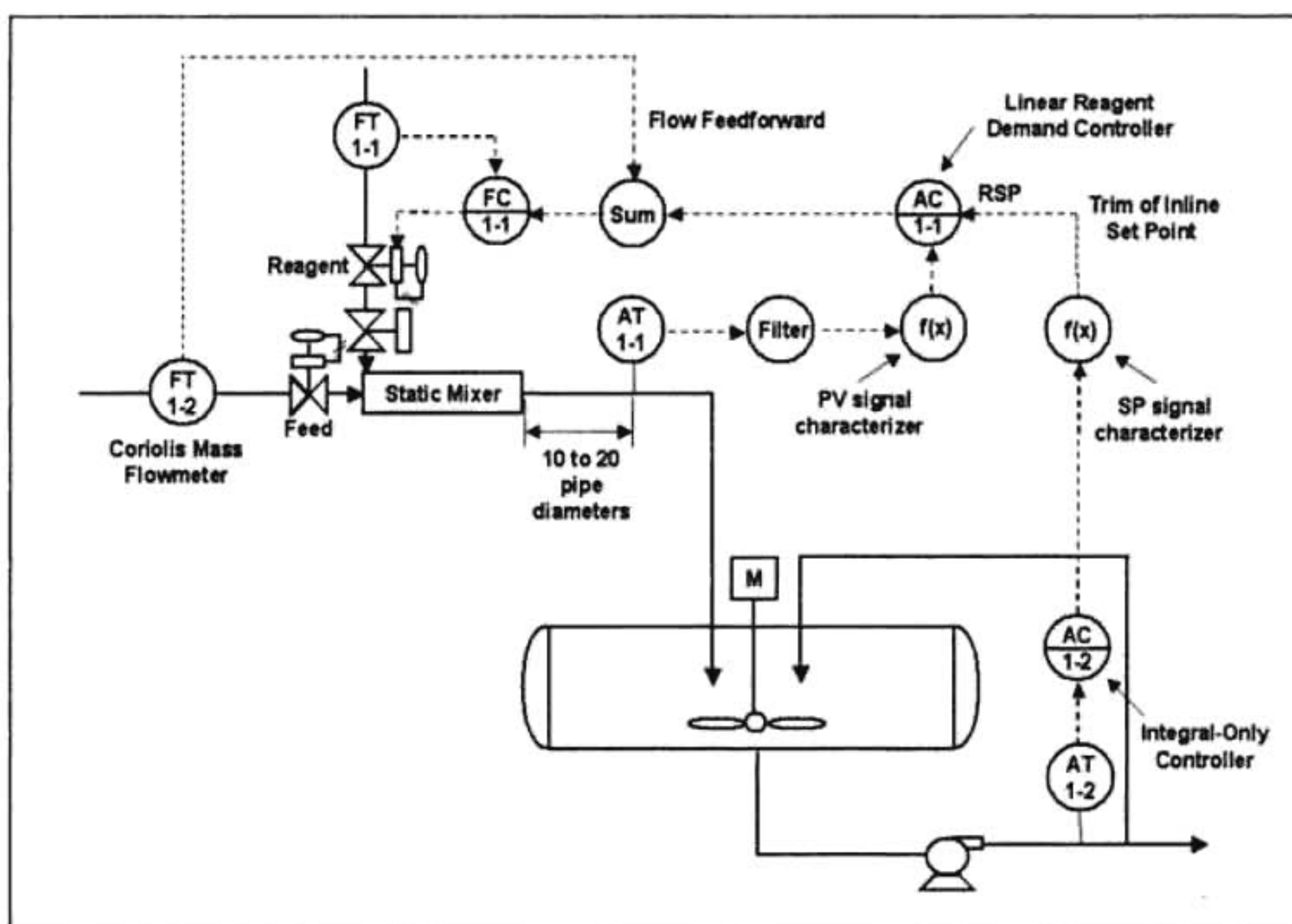


Figure 8-3b. Cascade Control of Vessel to Recirculation pH

#### 8-4. Linear Reagent Demand Control

For a linear reagent demand (LRD) controller, signal characterization or an online charge balance model is used to convert the controlled variable from pH to the X axis of the titration curve. For convenience, the abscissa is labeled 0% to 100% reagent demand. For the first stage, 0% of scale is set at a reagent to influent ratio of 0 and the 100% of scale set for a ratio that corresponds to the maximum overshoot in pH expected. For successive stages, the 0% is set at the extreme of the control band for the upstream stage. The set point must also be converted to % reagent demand so that it matches up with the new controlled variable. It is desirable to trend % reagent demand to show the benefits of using the LRD controller. If operations insist on a pH interface, the LRD controller can be kept as a detail display and a dummy pH controller presented to the operator. When the dummy controller is switched between the manual, auto, and cascade modes, the LRD controller mode is switched accordingly. In other words, the LRD controller mode tracks the pH controller mode. When the dummy controller is in manual and the operator changes the dummy controller output, the LRD controller output tracks it. However, when the dummy controller is in auto or cascade, the dummy controller output tracks the LRD controller output, and the LRD controller tracks the dummy controller set point after it has been converted to % reagent demand.



Users must be aware that the tuning settings of the dummy pH have no effect and the LRD open loop gain should be about 1 if the signal characterization curve is accurate.



**The operator may prefer to use a dummy pH controller even though the linear reagent demand controller is doing the work behind the scene.**

A horizontal shift in the titration curve can be handled by simple bias to the LRD controller set point to make the pH controller measurement better match up with its pH set point. This can be automated by using an integral-only master pH controller on a downstream volume or by passing the pH through a big dead time and filter block to create a dummy version of the horizontal tank pH controller. In either case, the master real or dummy pH controller slowly adjusts a bias to the set point of the secondary dummy pH controller.



***Use a real or dummy master pH controller to bias a dummy secondary pH controller set point to compensate for horizontal shifts in the curve.***

A change in the shape of the titration curve requires either an online adaptation of a charge balance model or identification of the titration curve. Both can be done online, particularly for a static mixer where the dynamics are fast and relatively well known. If a charge balance model is used to compute a curve online, the acid dissociation constant ( $pK_a$ ) closest to the pH set point can be slowly adjusted by model predictive control (MPC) whose controlled variable is the model pH and whose target is the actual pH. If a static mixer and accurate Coriolis mass flow measurements are installed for the influent or feed and reagent flows, the titration curve can be periodically identified online by ramping the reagent flow for a constant influent or feed flow as shown in Figure 8-5b.



***Use adaptation of the charge balance model pH or online identification of the titration curve to compensate for a distortion of the curve.***

The match between the curve used for the LRD controller and the real curve does not have to be perfect. Any sort of linearization is generally better than none at all. A LRD controller on the steep portion of the titration curve will see less noise and less of a limit cycle from stick-slip and will see the original equipment time constant by elimination of the acceleration. Thus, the user gets much more value of the investment made in a vessel volume to provide a process time constant that slows down



process dynamics [Ref. 8.1]. Furthermore, since the changes in dynamics have typically not been identified, the controller tuning settings are backed off from the optimum much more than are needed. In many cases, the loops end up in manual and the operator attempts to chase upsets, which is a fruitless task because of dead time and the high sensitivity and nonlinearity of the pH response.



**Controllers are excessively detuned or put in manual because the changes in process dynamics that cause oscillations have not been identified.**

In practice, three parameters are used to provide a first-order plus dead time (FOPDT) model of the process dynamics and to capture the essence of the process response. The most important of these is the loop dead time, which is the time delay between the change in a controlled variable (process output) after a change in a manipulated or disturbance variable (process input). If the dead time is zero and the measurement and valve resolution is unlimited, tuning is a nonissue and perfect control is possible. However, dead time always exists and is an accumulation of the pure delays from plug flow (transportation delays), valves (dead band and stick-slip), and digital devices (scan and execution time intervals) and the secondary time constant lags from mixing, actuator, sensors, and volumes in series [Ref. 8.2]. The next most important parameter is pH process gain, which is the final change in a pH for a given change in reagent flow. A high process gain (sensitivity) is desirable since it improves the inference of a process condition from a process measurement. However, a high process gain amplifies the stick-slip in valves and the noise from non-ideal mixing. The third parameter is the process time constant, which is the time to reach 63% of the final change in a controlled variable after the process has started to change (after the dead time). In plants, this time constant is rarely constant. For a large back mixed volume, it is essentially the residence time if the secondary lags take a back seat [Ref. 8.3]. However, the time constant seen by the controller is greatly reduced by the acceleration of the pH response on the steep portion of a titration curve, even though the actual process time constant has not changed. The controller only knows what it sees. Using the model parameters for controller tuning and loop performance and the effect of the nonlinearity of the titration curve on these parameters will be discussed in sections 8.10 and 8.11.

Changes in the FOPDT model parameters reveal changes in the raw materials, process, equipment, valves, and sensors. The size, direction,



and characteristics of these changes can provide a roadmap, knowledge of the terrain, and a route to more responsive controller tuning.



**A FOPDT model that consists of a process gain, time delay, and time constant can be used to describe the process response and calculate the controller tuning settings.**

Nearly all of the industrial adaptive controllers used to date in chemical processes require a rather long observation of changes in the process variable and show the results in terms of new tuning settings. The tuning rules are imbedded and usually unknown. The more prevalent adaptive controllers use pattern recognition and will, if necessary, increase the controller gain to induce oscillations. The size of the transients or oscillations and the time required for identification can translate to significant process variability and an adaptation rate that is slower than the rate of change of the process parameters. In fact, most adaptive controllers are playing catch-up even if they have seen the same situation a thousand times before. At best, these controllers provide a snapshot of the current tuning requirements and no real process insight as to where the process has been or where it is going. Also, sudden unexplained shifts in the tuning settings or bursts of oscillations reduce the operator's confidence and decrease the likelihood that the controllers will run in the adaptive mode and be used in future applications.



**Nearly all the adaptive controllers used to date are playing catch-up and do not reveal the process model or the imbedded tuning rules.**

Recently, adaptive controllers have been developed to rapidly identify a process model and provide process model parameters that can be displayed, trended, and diagnosed. Changes in the model parameters can reveal changes in feed or reagent compositions and installed valve characteristics and a coating of the sensor and plugging of the valve. Tuning rules can be selected based on user preference to match the process and the plant objectives. Furthermore, these controllers remember the results for similar conditions, eliminate repetitious identification, and take the initiative [Ref. 8.1].



**Changes in the process model can be used to predict and analyze changes in the influent, reagent, valve, and sensor.**



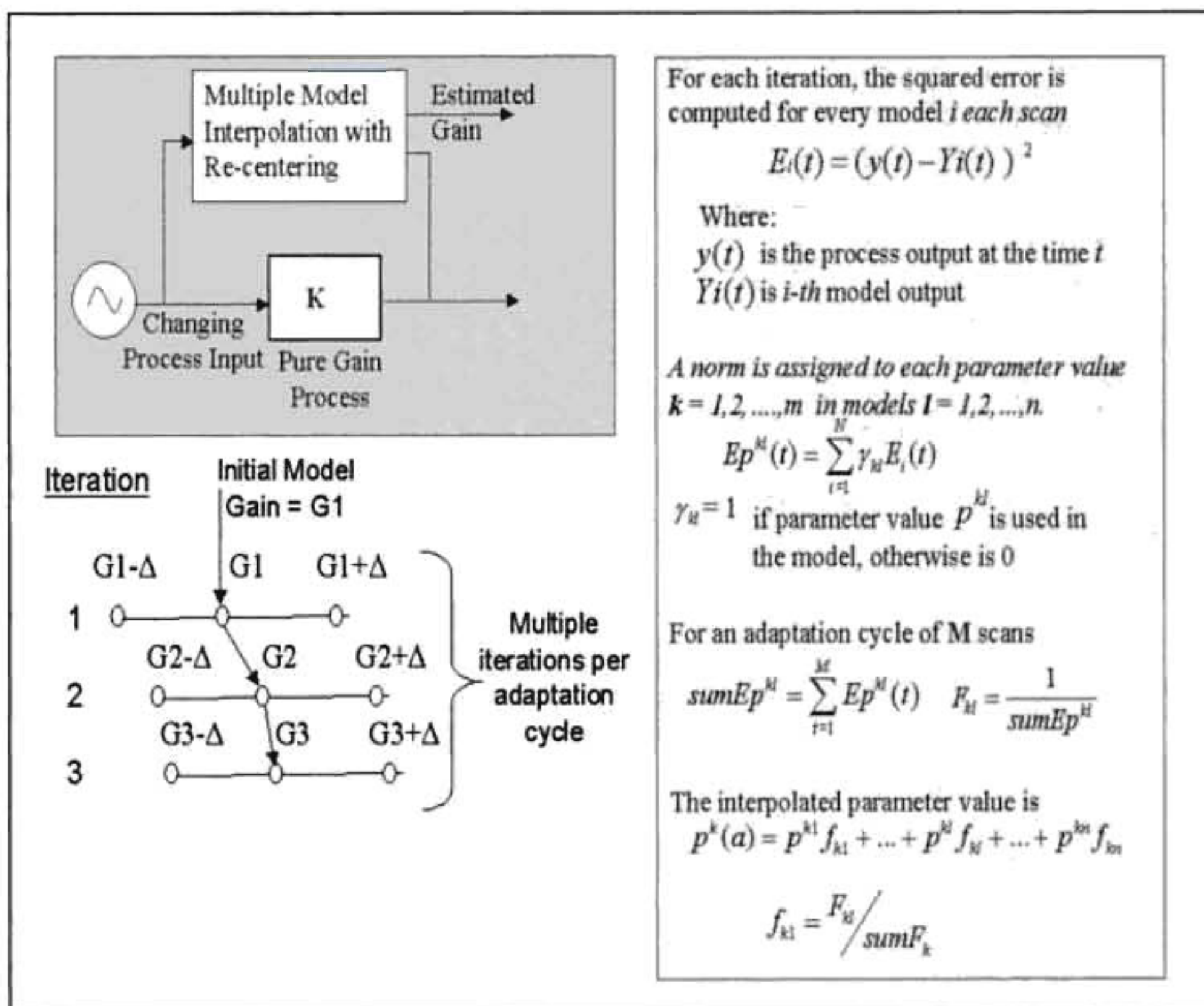


Figure 8-5a. New Adaptive Algorithm to Identify a Process Gain

The ramp should not start until the reagent pipe and injection lines are assured to be completely full of reagent. The ramp should go beyond the pH set point so the curvature is identified for overshoot. After the ramp is completed, the reagent flow should be initialized to the value identified to correspond with the desired pH set point to minimize the upset. If the ramp is fast compared to the size of the volume, the disturbance to the final pH should be negligible. The ramp can be periodically scheduled or initiated as a phase in a start-up or batch sequence. The accuracy of the curve is greatly improved by the use of Coriolis mass flowmeters and linear control valves. Figure 8-5b shows the use of a static mixer and the dynamic compensation of the ratio to identify a titration curve online.



**Use inline pH control, mass flowmeters, linear control valves, and dynamic compensation to automatically identify the titration curve online.**

The titration curve can also be identified during the normal pH adjustment phase of a batch operation. Here the ratio would be the totalized reagent flow divided by the batch mass. The synchronization of the ratio with the pH is more difficult because the dynamic compensation



becomes a function of the reagent delivery and mixing time delays and only the approach to the end point is identified since overshoot is not permissible.

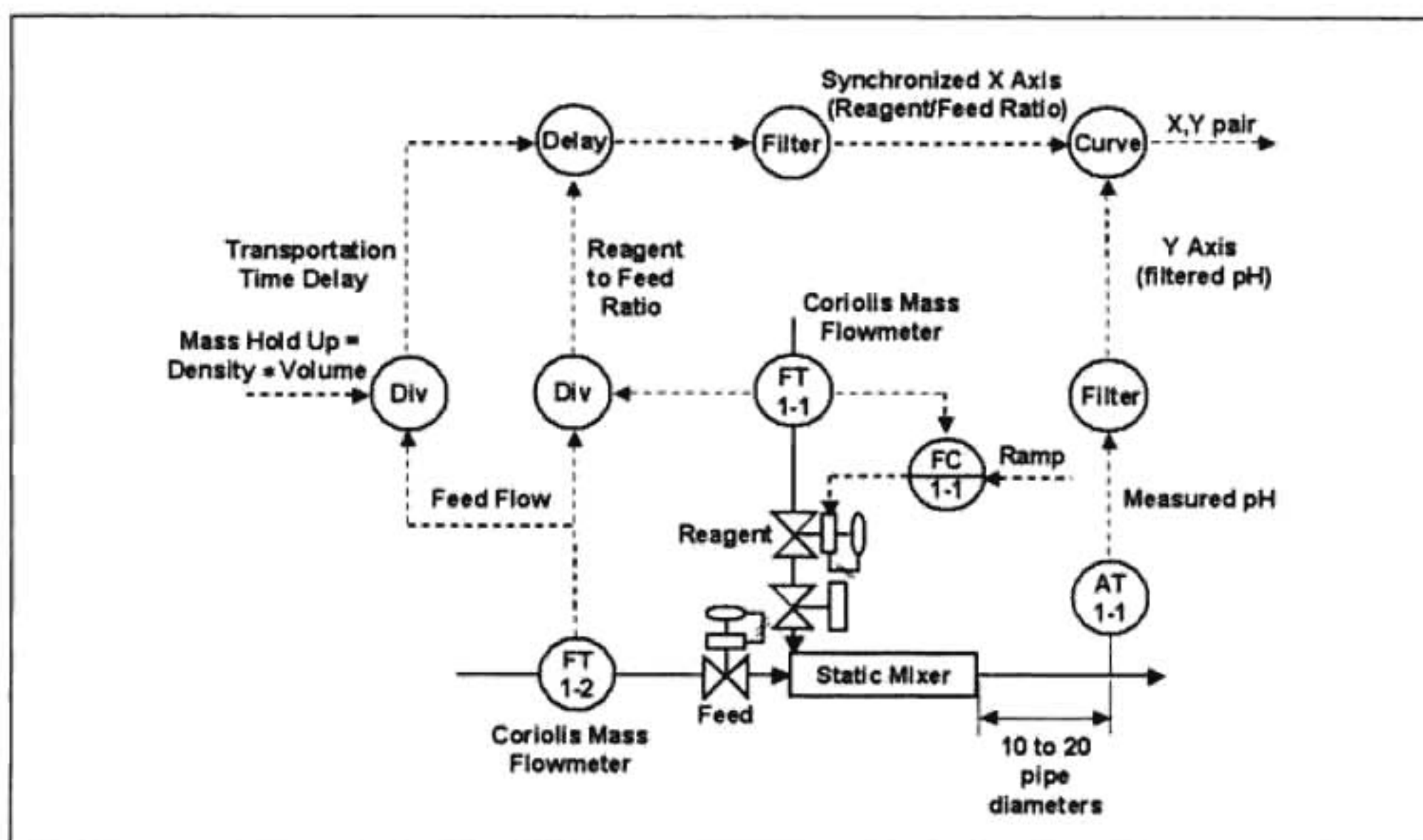


Figure 8-5b. Online Identification of a Titration Curve

The slope of the titration curve can be used to schedule the process gain and hence the controller gain. Alternatively, the curve can be used to convert the controlled variable to percent reagent demand per section 8-4. Either method frees up the adaptive controller to identify the changes rather than the whole shape of the curve. Finally, the curves and dynamic models can be used for dynamic online pH estimators, MPC, and real-time optimization of reagent consumption.



*Use gain scheduling or signal characterization based on the titration curve to free up an adaptive controller to find the changes in the curve.*

## 8-6. Advanced Batch Control

In a traditional batch sequence, the reagent is charged based on a preset total. There may be a dribble flow rate near the end to help improve the accuracy at the cutoff. Often the batch is held for lab analysis and manual trim adjustments. The lab sample should not be taken until the last drops of reagent for the main charge and each trim charge has gotten into the batch and been thoroughly mixed. The hold time for reagent delivery and mixing delays, manual sampling, lab analysis, and trim charges is considerable and can exceed the main charge time. To reduce the time

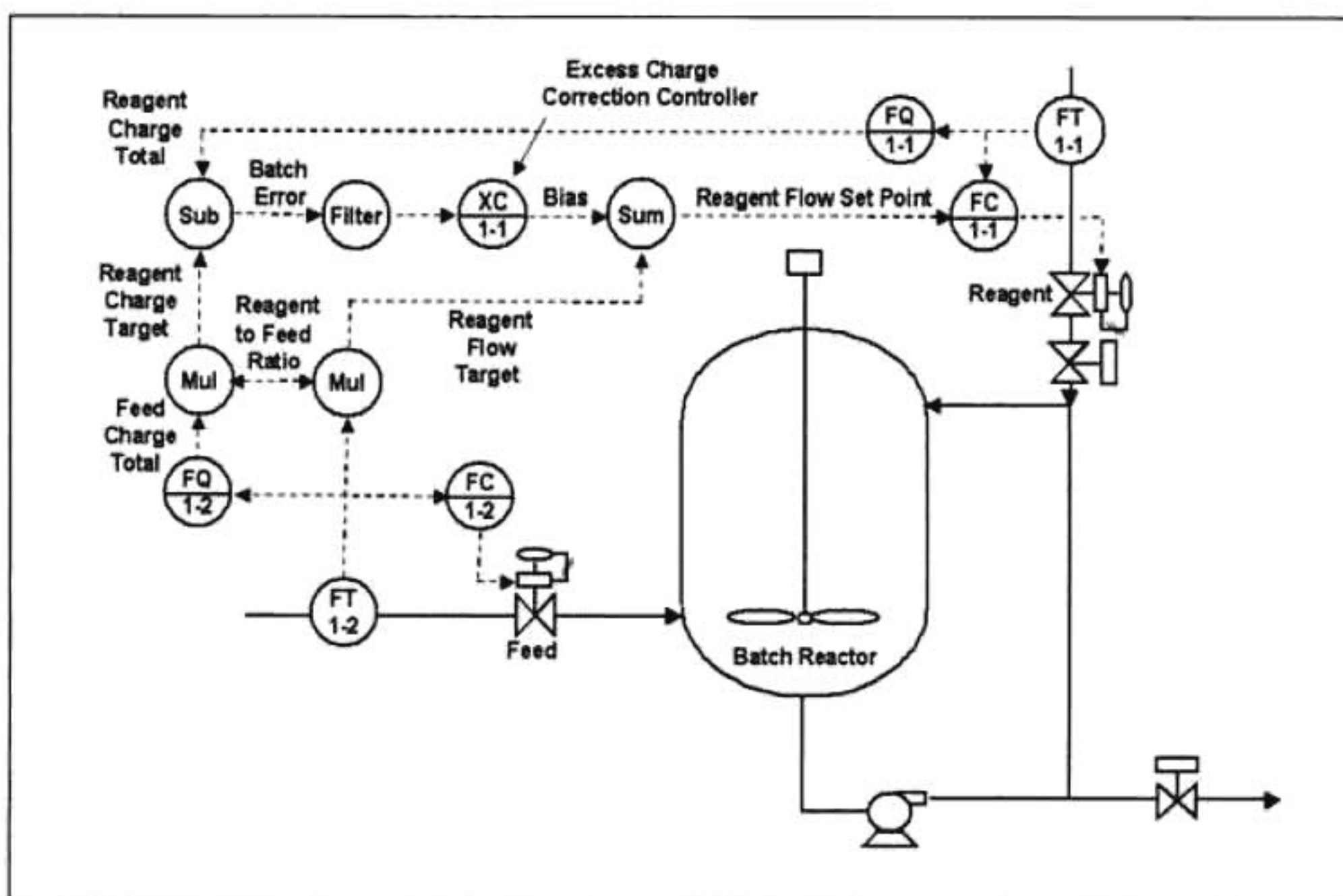


Figure 8-6a. Dynamic Correction of Mass Flow Ratio for Fed-Batch Operation

flowmeter and weigh tank errors, and upstream batch conditions. To eliminate chasing pH analysis errors, only half of the delta correction in charge is used.



*Half of the delta correction based on the pH analysis of the last batch can help correct for slowly changing errors and upstream conditions.*

An online pH measurement is necessary for variable and steep titration curves and the cases where large line sizes, high solids content, high temperatures, and special materials of construction preclude using Coriolis mass flowmeters. Using conventional pH feedback control is not normally advisable because the pH has an integrating response unless the reagent is consumed in the reaction. Reagent delivery and mixing time delays and reset action in a pH loop will cause considerable overshoot of the end point.

The fastest automated online pH adjustment consists of positioning the reagent valve wide open and shutting it when a predicted pH matches the batch end point. The pH measurement is velocity limited and filtered. The difference between the current value and a value passed through a dead time block is divided by the delay time (calculation time interval) of the dead time block to provide a rate of change of pH. The time delay should be large enough to improve the signal-to-noise ratio but small enough to not increase the system dead time by more than 10%. The predicted pH is



the present pH plus the pH rate of change multiplied by the system dead time, which is the total of the reagent delivery, mixing, measurement, and rate of change calculation time delays. It is important that the reagent delivery time delay be minimized by injecting the reagent into a feed line or into a recirculation line just before it enters the vessel as shown in Figure 8-6b.

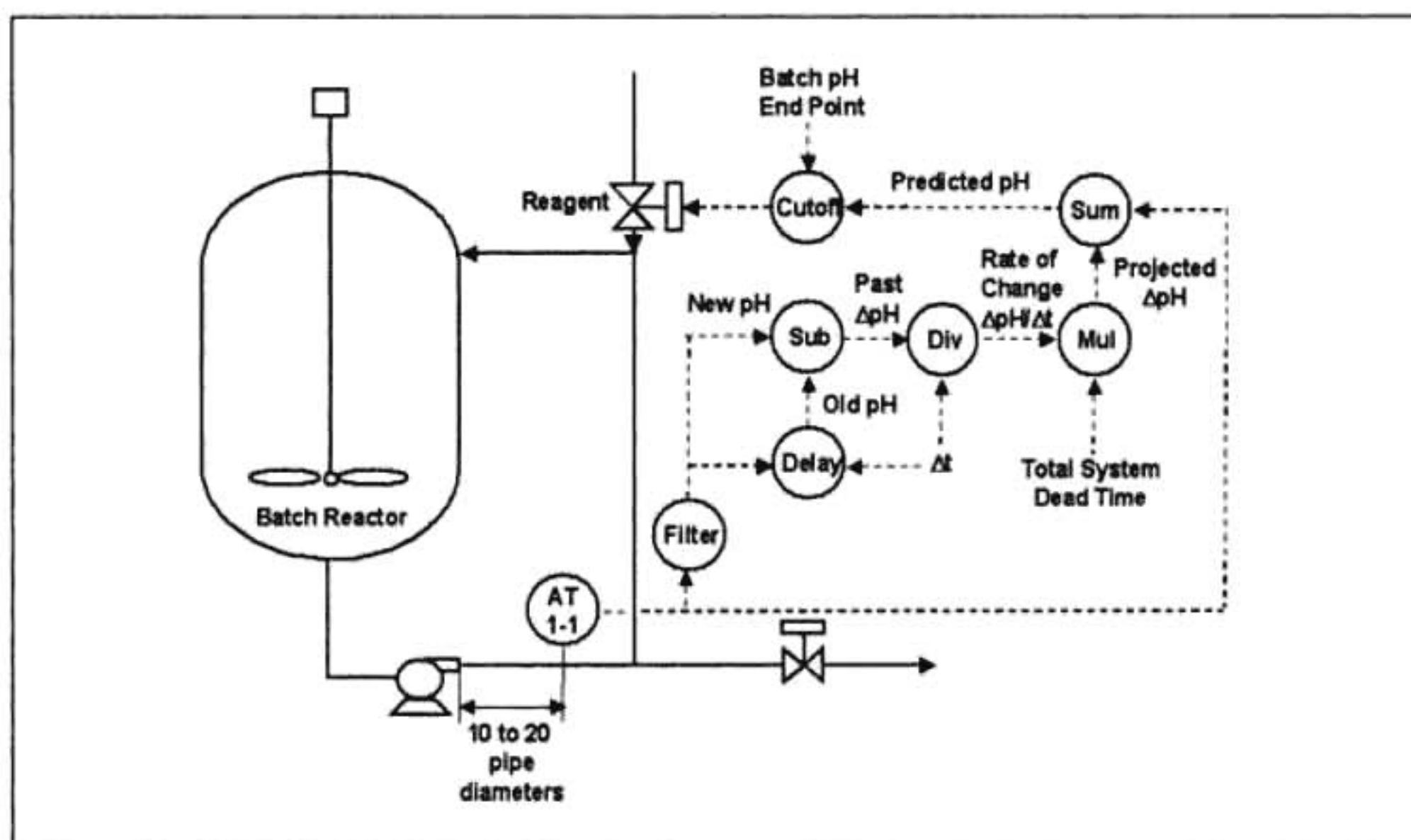


Figure 8-6b. Fast Charge Rate with Automated Cutoff Based on Predicted pH



*Use a wide open reagent valve that is shut based on a predicted online pH measurement to provide the fastest batch pH adjustment.*

A proportional plus derivative pH controller can be used for pulse width and amplitude modulation to mimic the lab titrations where the drop size and frequency is decreased as the vessel pH approaches the end point. The pulse width and amplitude is proportional to the pH controller output. The pulse cycle time (time between the start of successive pulses) is set equal to the system dead time, which increases the total dead time by 50%. A minimum pH controller output and hence pulse width and amplitude is selected that is a compromise between the need to minimize batch cycle time and prevent overshoot.



*Use pulse width and amplitude modulation of a proportional plus derivative controller output to mimic lab titration for batch pH control.*

For extremely variable titration curves, the titration curve can be identified online for linear reagent demand pH control if the pH extremes

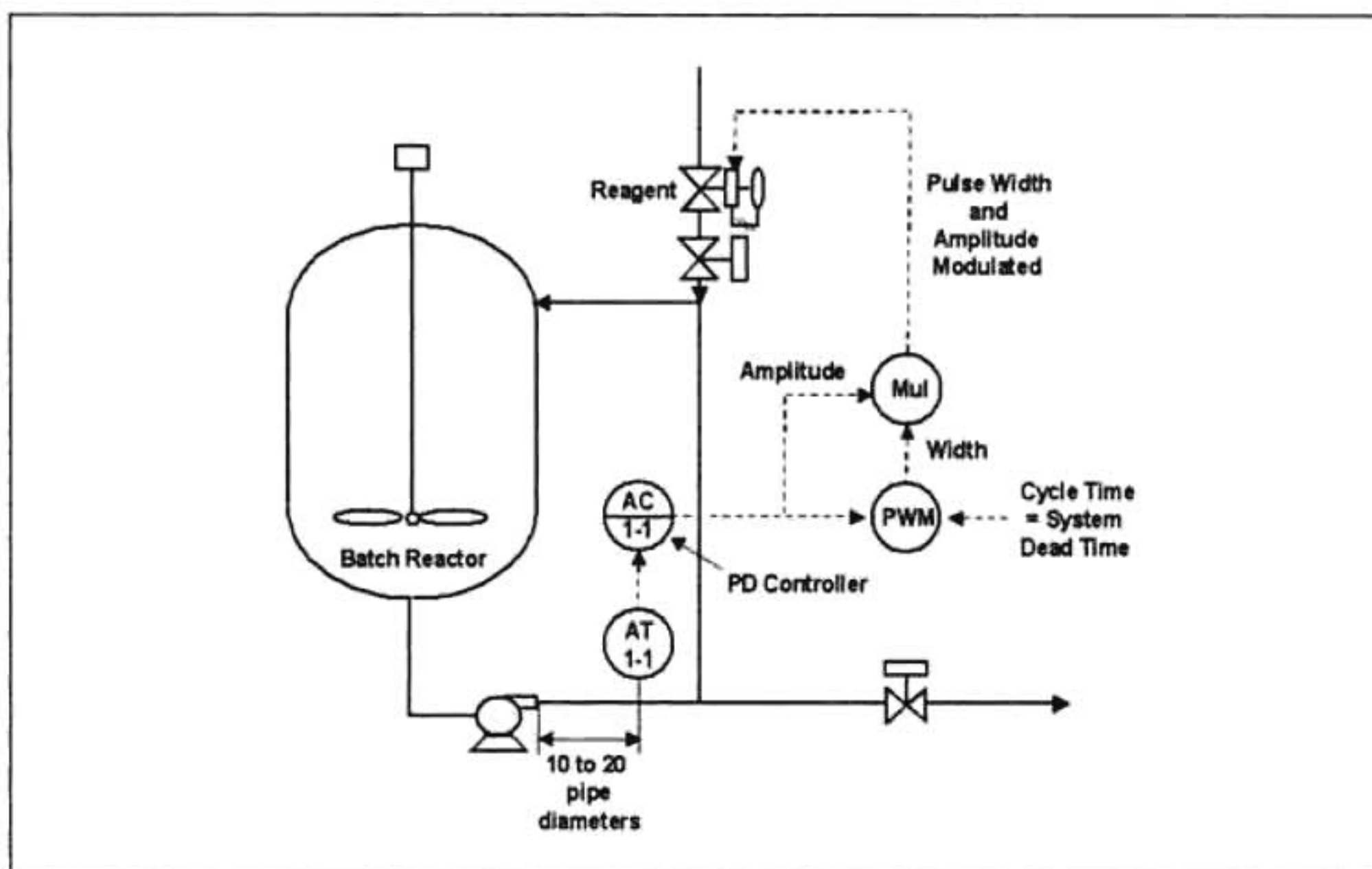


Figure 8-6c. Pulse Width and Amplitude Modulation to Mimic Lab Titrations

in the recirculation line do not cause quality problems. The master pH loop uses a linear reagent demand proportional plus derivative controller to help it recognize the distance to the end point. The future value of vessel reagent demand per section 8-7 can be used as the controlled variable. The secondary pH loop uses a proportional plus integral controller on a static mixer on the recirculation flow just before it enters the vessel. The remote set point of the secondary loop is the master controller pH output with a bias to keep the reagent valve open as the vessel pH approaches the end point. The titration curve is identified online at the static mixer as shown in Figure 8-6d. The reagent valve is shutoff when the master pH controller output equals the bias. The output limits of the master controller must match set point limits of the secondary controller that minimize quality and corrosion problems in the short section of line between the static mixer and the vessel.



*Use online titration curve identification and linear reagent demand pH control for extremely variable and sharp titration curvature.*

## 8-7. Dynamic Online pH Estimators

If the titration curve is fixed or identified or computed online and mass flowmeters are used, an online dynamic pH estimator can be readily constructed to provide a faster, smoother, and more reliable pH measurement. The ratio of reagent to feed mass flow is filtered and





*Use an online dynamic pH estimator to provide a much faster, smoother, and more reliable pH value if the open loop dead time and time constant are known and there are feed and reagent Coriolis mass flowmeters.*

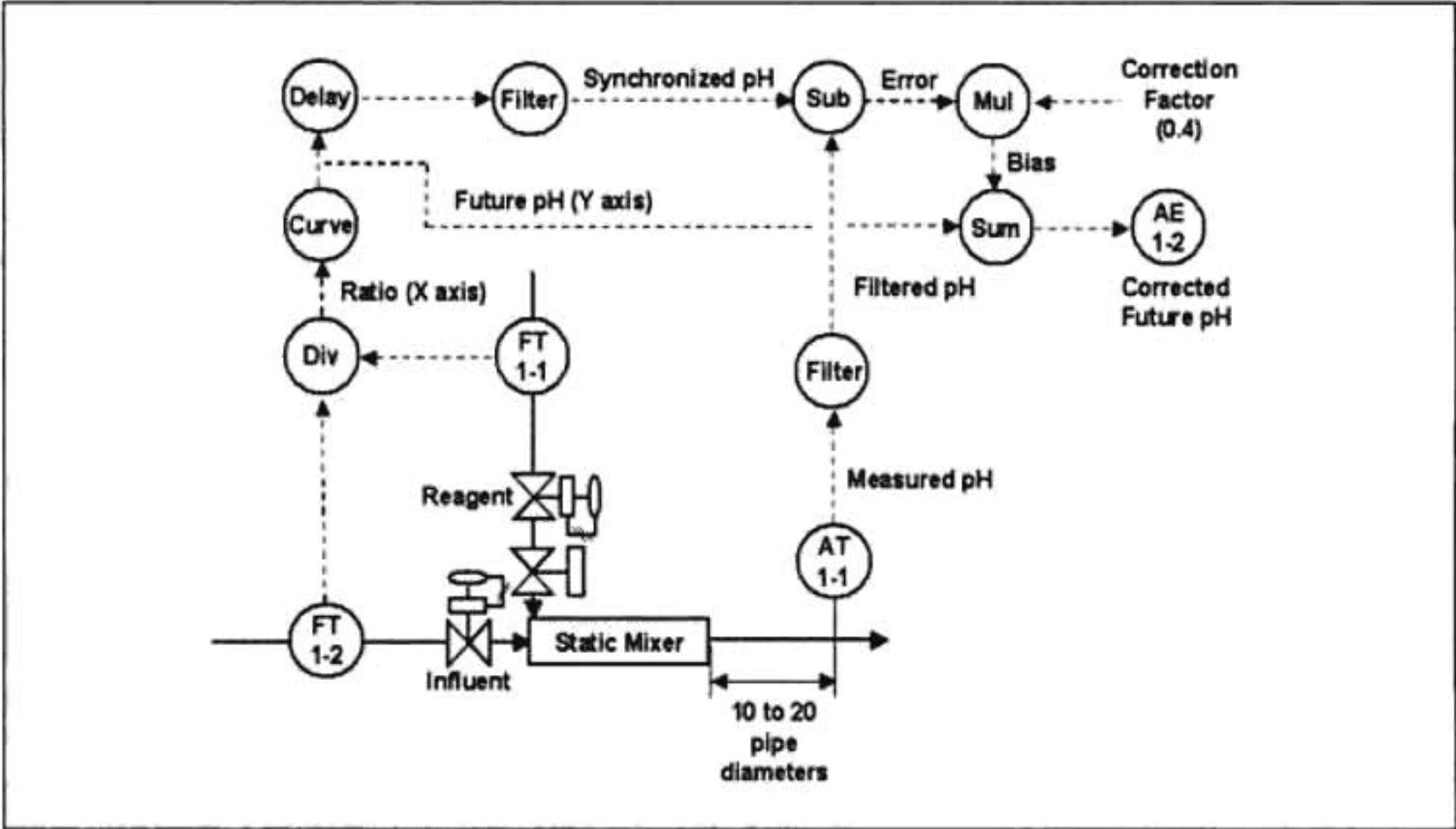


Figure 8-7a. An Online Dynamic pH Estimator for Future Value pH Control

8-8. Model Predictive Control

If the total loop dead time approaches or exceeds the open loop time constant, the pH loops interacts with another concentration or density control loop, or there is a need for constraint control, then model predictive control (MPC) should be used instead of PID control. The controlled variable should be linear reagent demand instead of pH because MPC is based on linear superposition [Ref. 8.4], and the titration curve drastically changes the process gain and severely distorts the process time constant as discussed in section 8.11 on loop performance. Online dynamic pH estimators can be used, but the future value should be the original reagent to feed ratio converted to percent reagent demand value as described in section 8.4. Industrial MPC software have built-in disturbance variables for feedforward control and optimization variables that can be used to maximize cross neutralization of waste streams or low-cost reagent while keeping the control valve for the more expensive supplemental reagent in a usable throttle range per the matrix shown in Figure 8-8a. If the feed is free to float within limits, the feed can be maximized based on low-cost or waste reagent availability per the matrix in Figure 8-8b.

A more common effective use of MPC is for the simultaneous coarse and fine reagent adjustments. In this case, the controlled variables are pH and

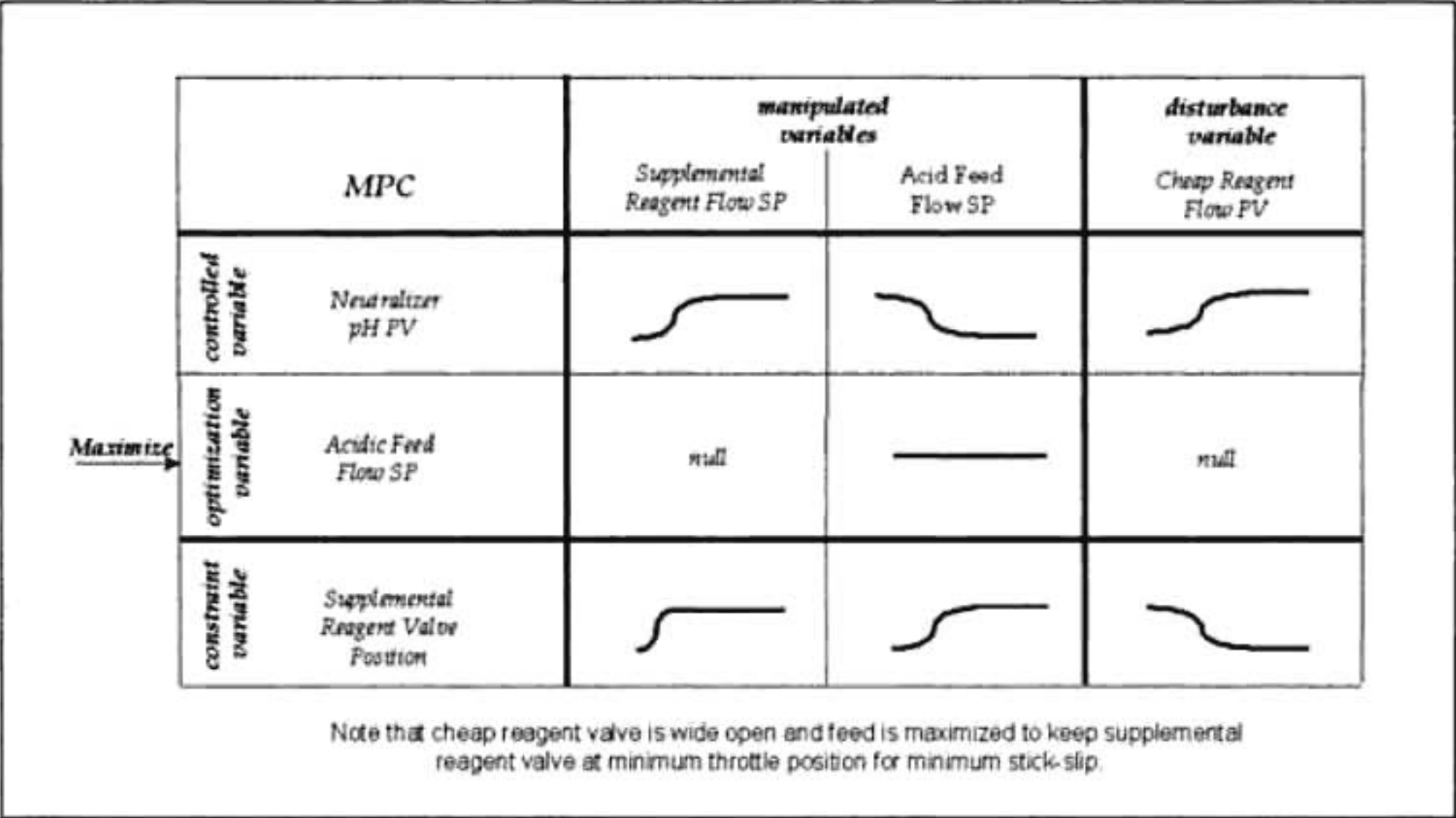


Figure 8-8b. Matrix for Minimization of Reagent Costs for Maximized Feed

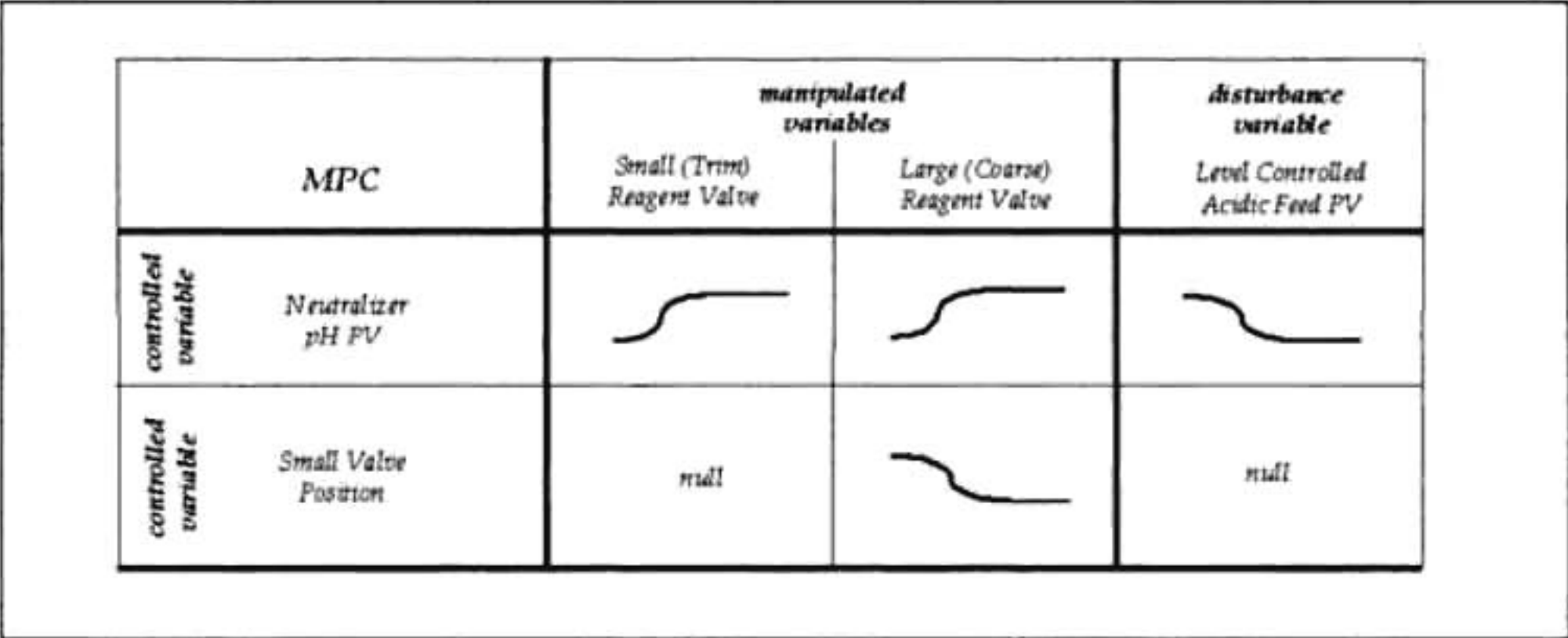



Figure 8-8c. Matrix for Simultaneous Coarse and Fine Reagent Adjustments

portion of the titration curve, the savings in reagent can be enormous as shown in Figure 8-9a.

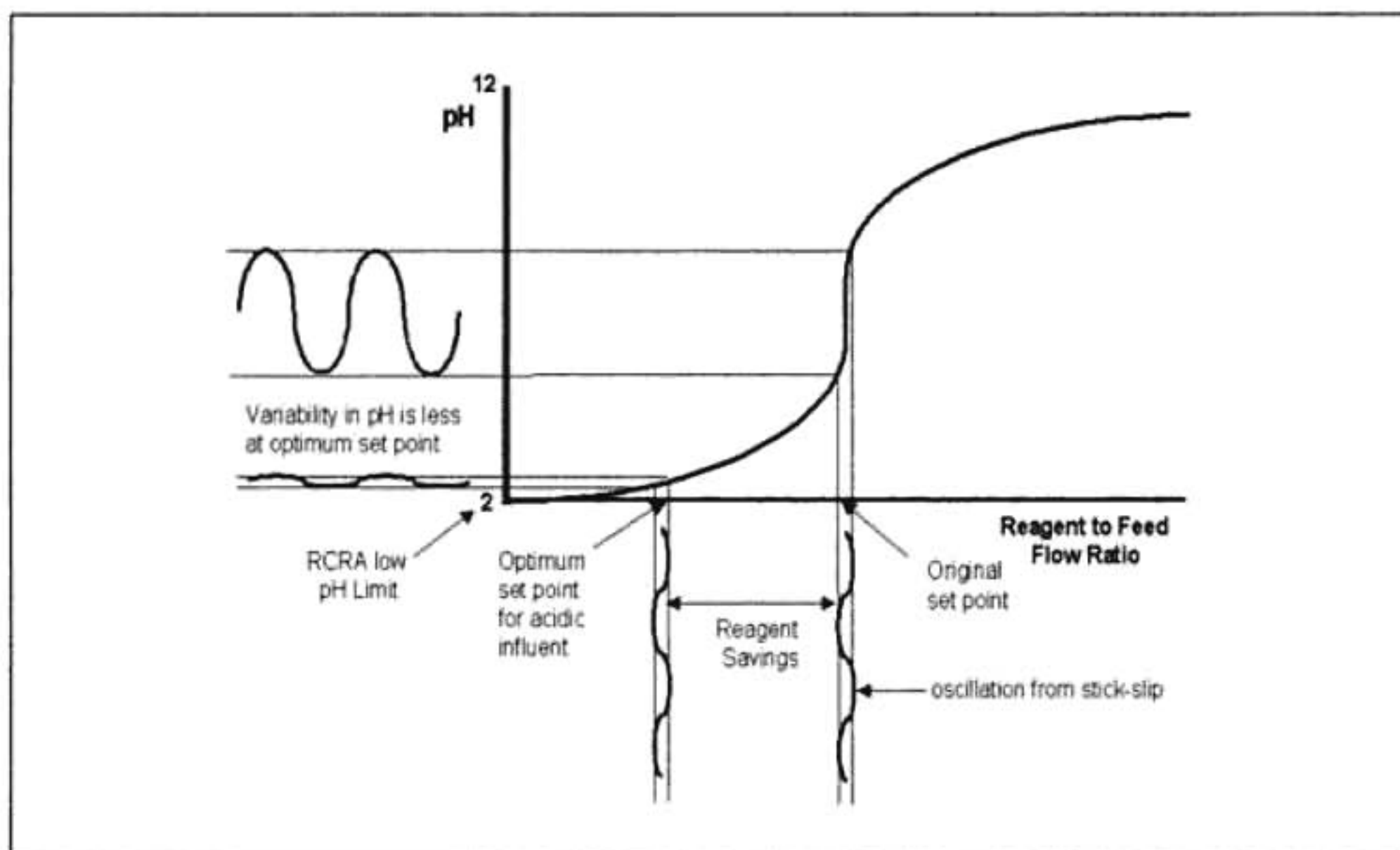


Use real-time optimization and variability projections to minimize reagent use if the titration curve can be identified or computed online.

### 8-10. Controller Tuning

pH controllers are perhaps the most difficult loop to tune because nothing is as it seems. The steep and flat portion of the curves can cause acceleration and deceleration, respectively, which distorts the time constant. Most pH control loops in service on strong acids and strong bases bounce back and forth between the flat portions of a titration curve.





**Figure 8-9a. Real-Time Optimization of Reagent Based on Variability Projections**

This nearly equal amplitude sustained oscillation is called a *limit cycle*. Automatic tuners generally require the loop to be at least somewhat calm and settled out near the set point. The limit cycle and extreme sensitivity (high process gain) causes most autotuners to abort or trigger an excursion that violates pH constraints.

The controller tuning settings and loop performance can be computed from a FOPDT approximation with three model parameters; open loop gain, open loop time constant, and total loop dead time. This method is helpful for designing new control systems and troubleshooting existing systems because it can pinpoint the source of a tuning and performance problem. Figure 8-10a shows the classical definition of the three parameters for a step change to a controller output with the loop in manual (open loop) for a self-regulating process, where pH reaches a new steady state, which is characteristic of continuous and fed-batch operation. Also shown is the ramp for an integrating response associated with a traditional batch operation and the acceleration for a positive feedback (runaway) response associated with an exothermic reactor. While pH systems do not have positive feedback, the approach to a steep portion of the titration curve mimics the runaway response.

The open loop gain ( $K_o$ ) is the product of the manipulated variable gain (valve gain), flow ratio gain, process variable gain, and the controlled variable gain (measurement gain) as detailed in Equations 8-10a through 8-10f. In the literature, the open loop gain is called the process gain, and little is done to analyze or distinguish the individual gains. A closer look at the contributions from each component in the loop helps to understand

The ultimate gain ( $K_u$ ) is equal to the inverse of the product of the open loop (static) gain ( $K_o$ ) and the amplitude ratio at a phase shift of  $-180^\circ$  ( $AR_{180}$ ) [Ref. 8.3].

$$K_u = \frac{1}{K_o * AR_{-180}} \quad (8-10m)$$

The amplitude ratio for a sine wave applied to self-regulating process with an open loop negative feedback time constant ( $\tau_o$ ) is [Ref. 8.3]:

$$AR_{180} = \frac{1}{[1 + (\tau_o * \omega_n)^2]^{1/2}} \quad (8-10n)$$

If Equation 8-10n is substituted into Equation 8-10m, we have the ultimate gain as a function of the open loop negative feedback time constant ( $\tau_o$ ) and the natural frequency ( $\omega_n$ ).

$$K_u = \frac{[1 + (\tau_o * \omega_n)^2]^{1/2}}{K_o} \quad (8-10o)$$

Since the natural frequency in radians per minute ( $\omega_n$ ) is  $2\pi$  divided by the ultimate period ( $T_u$ ), we can express the ultimate gain ( $K_u$ ) as a function of the ultimate period.

$$K_u = \frac{[1 + \{(\tau_o * 2 * \pi)/T_u\}^2]^{1/2}}{K_o} \quad (8-10p)$$

For a time constant much larger than the time delay ( $\tau_o \gg \tau_d$ ), the ultimate gain is:

$$K_u = \frac{2 * \pi * \tau_o}{K_o * T_u} \quad (8-10q)$$

Since for this case the ultimate period is about 4 times the time delay ( $T_u \cong 4 * \tau_d$ ), the ultimate gain can be simplified to a ratio of the time constant to time delay.

$$K_u = 1.6 * \frac{\tau_o}{K_o * \tau_d} \quad (8-10r)$$



Since the controller gain is a factor of the ultimate gain ( $K_c = 0.25 \cdot K_u$ ), the controller gain is proportional to the time constant and inversely proportional to the time delay and the open loop gain.

$$K_c = 0.4 * \frac{\tau_o}{K_o * \tau_d} \quad (8-10s)$$

If the time delay is much larger than the time constant ( $\tau_d \gg \tau_o$ ), it can be shown that Equation 8.10s reduces to the ultimate gain being the inverse of the open loop gain. This relationship can also be realized from the amplitude ratio being 1 for a pure time delay.

$$K_c = 0.25 * \frac{1}{K_o} \quad (8-10t)$$

The phase shift ( $\phi$ ) from a time delay is [Ref. 8.3]:

$$\phi = -360 * f_n * \tau_d \quad (8-10u)$$

If we substitute in the relationship between natural frequency in cycles per minute and the ultimate period ( $f_n = 1/T_u$ ), we have:

$$T_u = (-360/\phi) * \tau_d \quad (8-10v)$$

For a time constant much larger than the time delay, there is a -90 phase shift from the time constant, which leaves only -90 phase shift ( $\phi$ ) needed from the time delay to reach the -180 total phase shift, the ultimate period becomes simply 4 times the time delay.

For  $\tau_o \gg \tau_d$ :

$$T_u = 4 * \tau_d \quad (8-10w)$$

If on the other hand, the time constant is so much smaller than the time delay that essentially all -180 phase shift ( $\phi$ ) comes from the time delay, the ultimate period approaches 2 times the time delay.

For  $\tau_d \gg \tau_o$ :

$$T_u = 2 * \tau_d \quad (8-10x)$$

The following curve fit shows how the ultimate period changes from a multiple of 2 to 4 of the time delay and a function of the relative sizes of the time constant and time delay.

$$T_u = 2 * \left[ 1 + \left[ \frac{\tau_o}{\tau_o + \tau_d} \right]^{0.65} \right] * \tau_d \quad (8-10y)$$

where:

- $AR_{-180}$  = amplitude ratio at a phase shift of  $-180^\circ$
- $K_c$  = controller gain
- $K_o$  = open loop static gain
- $K_u$  = ultimate gain
- $\phi$  = phase shift from time delay (degrees)
- $\tau_d$  = total time delay (dead time) (minutes)
- $\tau_o$  = open loop time constant (minutes)
- $T_i$  = controller integral time (minutes per repeat)
- $T_d$  = controller derivative time (minutes)
- $T_u$  = ultimate period (minutes)
- $\omega_n$  = natural frequency (radians per hr)

More often than not the pH controller is manually tuned. A closed-loop damped oscillation method is favored because the controller can already be oscillating, it forces the user to back off on reset action and to first find the controller gain, it includes any special features of manufacturer's PID algorithms and the dead time from valve dead-band and stick-slip, and it can be used to tune a master controller for an oscillating secondary loop. However, it is critical to remember that this is a damped oscillation method and the nearly equal amplitude oscillations normally associated with this method must be avoided because these can be caused by a limit cycle from valve stick-slip or the nonlinearity of the titration curve. Many users see a limit cycle and think they have the ultimate gain when in reality these cycles are caused by a wide range of controller gains.

A list of steps for this the closed loop damped oscillation method is as follows:

#### Closed-Loop Damped Oscillation Tuning Method:

1. Put the controller in automatic at its normal set point. If it is critical to not make big changes in the controller output, temporarily narrow the controller output limits for this test to restrict valve movement.
2. Increase the reset time by at least a factor of 10 and trend record pH, controller output, and reagent flow.



3. Add filter to keep the high frequency output fluctuations from noise within the stick-slip of the valve to prevent the valve from reacting to noise. Keep this filter after tuning.
4. Bump the set point and increase or decrease the controller gain until there are quarter amplitude oscillations. Note the period of these oscillations. For gain settings larger than 1, the oscillation will be more recognizable in the controller output. Make sure the controller output stays within a good throttle range.
5. Cut the controller gain in half to help smooth out the damped oscillation (this corresponds to about  $\frac{1}{4}$  the ultimate gain). If the pH can move to a steep part of the titration curve, the controller gain must be further decreased per the ratio of the slopes.
6. Estimate the ultimate period as about half the quarter amplitude period and use Equations 8-10j through 8-10l to estimate the integral and derivative time settings.



*If the pH can move to a steeper part of the titration curve, the controller gain must be decreased by a factor equal to the ratio of the slopes.*



A closed-loop damped oscillation method for tuning allows a controller to already be oscillating, forces the user to back off on reset action and to first find the maximum controller gain, includes the special features of manufacturer's PID algorithms and the dead time from valve dead-band and stick-slip, and can be used to tune a master controller for an oscillating secondary loop.

For traditional batch pH control, the reagent is charged after the feed with the drain valve closed; consequently, the composition response is integrating to a step change in reagent flow. There is no negative feedback, and hence, no self-regulation. The composition response will ramp until a physical limit is reached but the movement of the operating point from the steep to the flat portion of the titration curve may give the false impression that the pH is "lining out" and the process is self-regulating. The ultimate period can be estimated by Equation 8-10z for batch pH control. Note that the ultimate period is equal to about four times the dead time for a large dead time to time constant ratio. For a small dead time to time constant ratio, the ultimate period will be significantly larger for batch control. For example, if the dead time is 0.1 minute and the time constant is 1 minute, the ultimate period for continuous pH control is about 4 times the dead

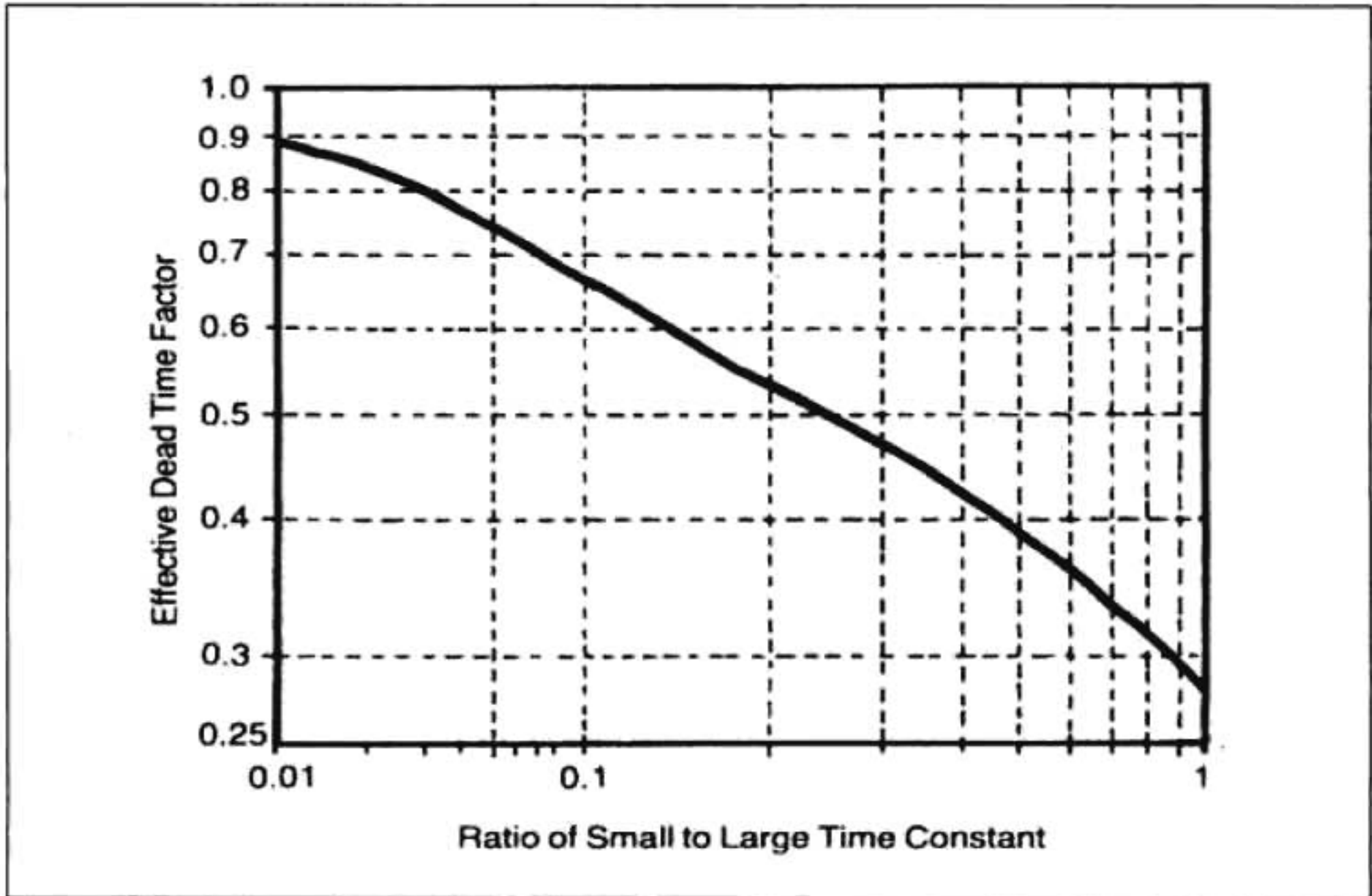


Figure 8-10b. Increase in Fraction of Time Constant Converted to Dead Time for a Decrease in the Small to Large Time Constant Ratio

load upset and is important if short-term environmental violations or excursions that trigger adverse reactions are a concern. The integrated error is the area between the pH and set point on a trend and is a measure of the amount of off-spec material created. Note that all error calculations must first be done in terms of reagent error that then must be translated from the X to the Y axis of the titration curve to get the pH error.

Since a controller cannot either sense or compensate for an upset until after one dead time, the minimum peak error ( $E_x$ ) is the exponential response after one dead time. This is the best a feedback controller can do. In industrial systems, the actual peak error will be much larger because of less-than-ideal controller tuning and nonlinearities.

$$E_x = [1 - e^{(-\tau_d / \tau_o)}] * E_o \tag{8-11a}$$

If the time delay is less than the time constant, we can simplify the relationship.

For  $\tau_d < \tau_o$ :

$$E_x = \frac{\tau_d}{\tau_o + \tau_d} * E_o \tag{8-11b}$$



- $E_o$  = open loop reagent error for controller in manual (kg per minute)  
 $E_x$  = peak reagent error (kg per minute)  
 $\tau_d$  = total time delay (dead time) (minutes)  
 $\tau_o$  = open loop time constant (minutes)  
 $T_i$  = controller integral time (minutes per repeat)



**The integrated error and amount of off-spec material in most well-designed pH control systems is proportional to the total loop dead time squared.**

The most frequent cause of problems for a pH control system that is dead time dominant (dead time much larger than the open loop time constant) with a large magnitude of dead time are miscues in the design of the reagent system. Reagent delivery delays can be truly horrendous from back filled or partially filled reagent pipe, injection tubes, and dip tubes. Less often, but still likely, are the misguided attempts to control the pH in sumps and ponds where the dead time is ridiculously large from a poorly mixed large volume.

For buffered inline systems with a clean spherical bulb in dilute aqueous solutions, the process variable filter time and the glass electrode time constant are small. This is the one case where a well-designed pH control system ends up dead time dominant. However, the magnitude of the dead time is small and consequently the integrated error is very small. The peak error for a step disturbance would be the open loop error. However, most upsets are not a true step change but have a time constant. Even a flow upset from a step change in a flow set point has a time constant because of the reset action in the flow controller. The effect is similar to a process time constant in that both slow down the excursion rate and the minimum peak error corresponds to how far the process deviates in one dead time. If the time constant of the disturbance is larger than the total loop dead time, then Equations 8-11a through and 8-11c can be used with the disturbance time constant substituted for the open loop time constant.

For strong acid-base inline systems, a large digital filter is needed to average out the oscillations and smooth out the noise caused by the high process sensitivity. The filter time constant is the largest time constant in the loop and is effectively the open loop time constant shown in the equations in this section. While these equations are valid because the filtered peak error is decreased as the filter time constant is increased, you are seeing an attenuated version of the real world. If you were to take this to its extreme, you would set a filter time so large that the trend would be a straight line. To get the actual unfiltered excursion, Equation 5-3j for the

amplitude ratio can be solved for the input amplitude. The result is Equation 8-11h, where the input amplitude is the actual peak error, and the output amplitude is filtered peak error.

$$E_x = E_f * \frac{2 * \pi * \tau_f}{T_o} \quad (8-11h)$$

where:

- $E_f$  = filtered peak reagent error (kg per minute)
- $E_x$  = actual peak reagent error (kg per minute)
- $T_o$  = period of oscillation (minutes)
- $\tau_f$  = process variable filter time constant (minutes)

The errors predicted in terms of dead time to time constant ratios are the best case whereas in reality, particularly for pH loops, the controller tuning sets the performance. Thus, a poorly tuned control on an expensive well-mixed vessel with a great valve and reagent system, will behave badly. The fact that the pH loop sees an accelerating pH as it move on the steep part of the titration curve complicates tuning. Equation 8-11i, which is developed from the exponential response of a time constant, can be used to estimate the time constant seen by the pH loop. The 100% and 63% values of the open loop pH error from an upset are marked on the titration curve and translated to equivalent open loop reagent errors ( $E_{100}$  and  $E_{63}$ ) as shown in Figure 8-11a. The original time constant is multiplied by the natural logarithm of 1 minus the ratio of the 63% to 100% reagent error ( $E_{63} / E_{100}$ ). The effect can be quite severe. For example, the pH loop sees just a 0.04 minute time constant for a 19 minute process time constant from a well-mixed vessel for a strong acid and strong base system.

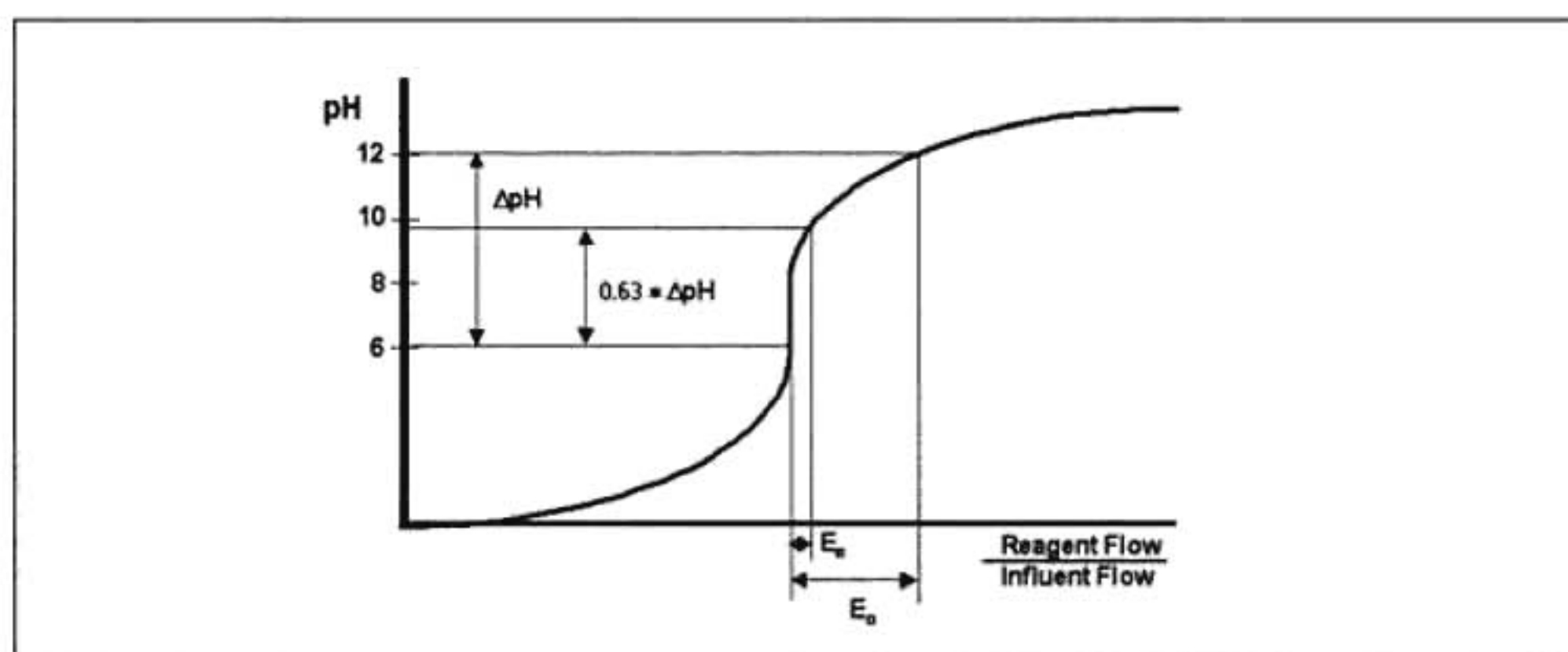


Figure 8-11a. Translation of Open Loop Errors to Find Time Constant Seen by a pH Loop



The equipment should minimize the magnitude of the process dead time from a plug flow volume. This can be realized by maximizing the back mixing in a vessel or minimizing the length of an inline system and avoid putting loops on horizontal tanks and sumps.

The reagent delivery system should minimize transportation delay, flatten the titration curve, and provide a high turbulent reagent flow free of solids or gas. Practically this is achieved by pre-dilution of the reagent, selecting a weak acid or base with a dissociation constant close to the set point, keeping reagent systems full of reagent, and premixing the reagent into a high feed or recirculation stream close to the point of entry into the vessel.

For control system selection, the main questions pertain to the number of stages, type and size of equipment, location of the set points, and the most appropriate advanced control technology. The question as to the number of stages and type of equipment mostly applies to neutralization systems. For pH control of unit operations for production such as fermentation, reaction, and crystallization, the process equipment is predetermined.

The traditional rule has been that one stage of neutralization is required for every 2 pH units the influent pH is away from the set point. For example, to go from an influent at 1 pH to a set point of 7 pH requires three stages of neutralization. A more exact rule would add another stage of neutralization if the control valve resolution was estimated to be more than half the allowable reagent error for the control band. This means that control valves with very low stick-slip and advanced control strategies that allow manipulation of a trim and a coarse valve on the same stage could eliminate a stage of neutralization.

As far as the set point is concerned, it should be located on the flattest part of the titration curve that keeps the pH within the control band. The oscillations will often be less and the whole control problem reduced if the pH is shifted away from the neutral point towards the edge of the control band.

The least expensive equipment with the least total dead time is the inline pH system. Even though it doesn't have the good dead time to time constant ratio of the well-mixed vessel, the integrated error and the amount of off-spec material is much less. The system is also easier to tune once it is realized that strong acid-base systems require a pH signal filter time of 0.2 minutes. Figure 8-12a shows that while the inline system has a high peak error for a step upset, it recovers much faster than a well-mixed vessel. The figure also shows how disastrous a horizontal vessel is for pH control. There is not enough room on the trend to show the ridiculously slow and severe oscillations from a sump.

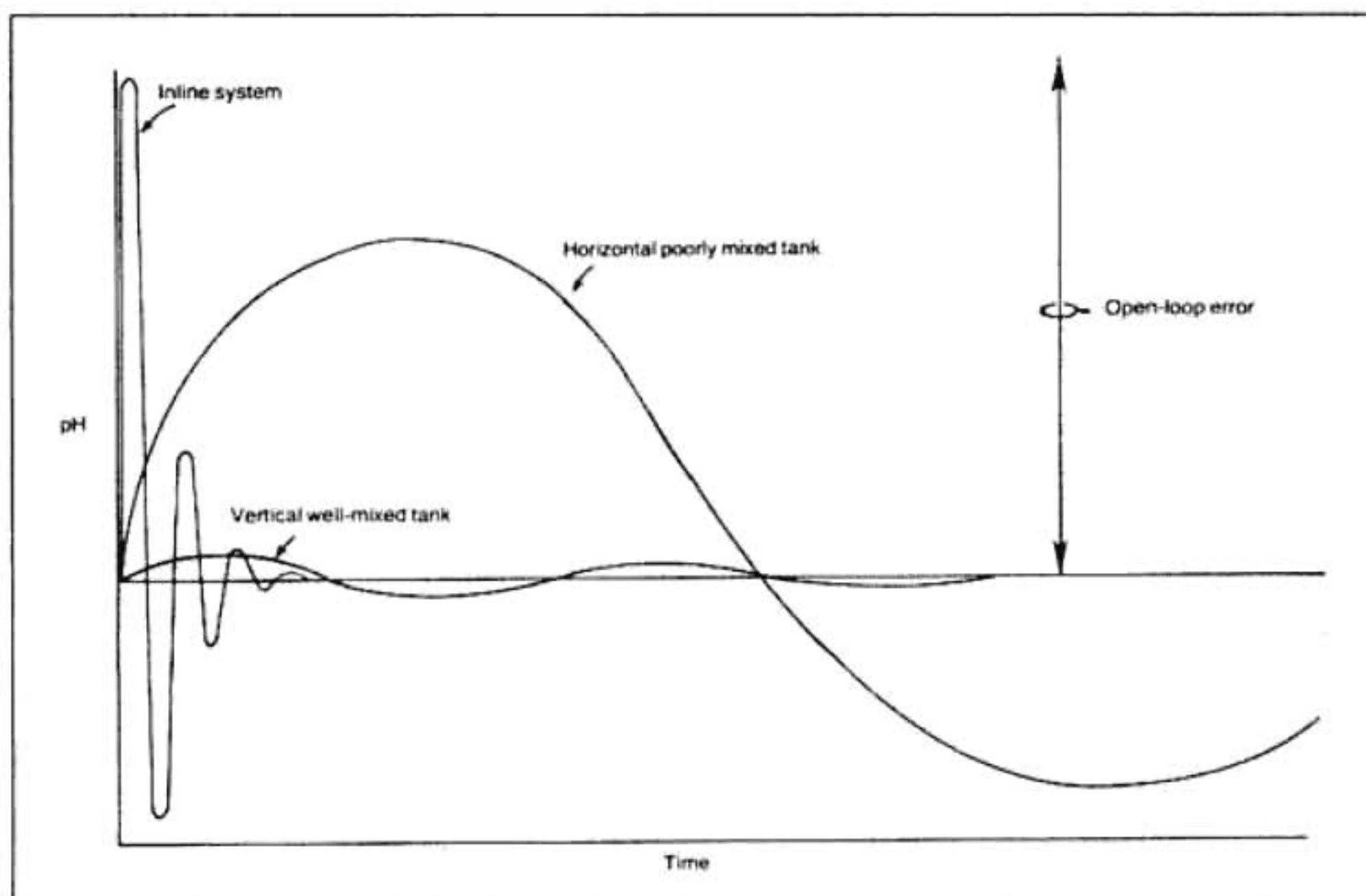


Figure 8-12a. Performance of Inline System, Well-Mixed Vessel, and Horizontal Tank

The inline system must have a volume downstream sufficient enough to attenuate the oscillations. Equation 5-3j can be used to estimate the volume size for the worse case oscillations. The inline system can take many forms. It can be a static mixer, centrifugal pump, or a dynamic inline mixer that has high-speed rotating blades. It can be located on a feed or recirculation stream and can be set up for online identification of the titration curve. An inline system should be used for the first stage rather than the final stage.

For multiple stages, the period of oscillations must be different by a factor of 5 or more to eliminate resonance. This means the total dead time from each stage and the volume for each well-mixed vessel should differ by more than a factor of 5. The smallest volume should be first so that this stage that bears the brunt of the assault creates the least amount of off-spec product. The biggest control valve should be on the first stage and the smallest on the last stage. The set point for the first stage should take the pH the furthest distance on the titration curve.

If Coriolis and magnetic flowmeters are installed to measure the reagent and influent flows, cascade control, flow feedforward, and online identification of a titration curve should be utilized to facilitate start-up and recovery from the flat portions of the titration curve and improve over system performance and knowledge. If the titration curve is relatively fixed or can be calculated or identified online, linear reagent demand control should be used to suppress oscillations and noise and restore



# **Appendix A: Suggested Readings**

## Appendix A

### Suggested Readings

#### Handbooks

McMillan, Gregory, K., *Process/Industrial Instrumentation and Control Handbook*, 5<sup>th</sup> edition, McGraw-Hill, 1999.

#### Textbooks

Bates, R.G., *Determination of pH Theory and Practice*, Reprint via ProQuest UMI "Books on Demand", John Wiley and Sons, 1964.

Blevins, Terrence L., McMillan, Gregory K., Wojsznis, Willy K., and Brown, Michael W., *Advanced Control Unleashed – Plant Performance Management for Optimum Benefits*, ISA – The Instrumentation, Systems, and Automation Society, 2003.

Galster, Helmuth, *pH Measurement – Fundamentals, Methods, Applications, Instrumentation*, VCH (Out of Print), 1991.

McMillan, Gregory, K., *A Funny Thing Happened on the Way to the Control Room*, Reprint via ProQuest UMI "Books on Demand", ISA – The Instrumentation, Systems, and Automation Society, 1989.

McMillan, Gregory, K., *Good Tuning: A Pocket Guide*, ISA – The Instrumentation, Systems, and Automation Society, 2003.

Shinskey, F.G., *pH and pION Control in Process and Waste Streams*, John Wiley and Sons, 1973.

Wescott, Clark, C., *pH Measurements*, Academic Press, 1978.

#### Articles

Frant, Martin, S., "How to Measure pH in Mixed and Non-aqueous Solutions", *Today's Chemist at Work*, June 1986.

McMillan, Gregory K., "Understand Some Basic Truths of pH Measurement", *Chemical Engineering Progress*, October 1991.

McMillan, Gregory K., "pH Measurement: The State of the Art", *InTech*, February 1993.

McMillan, Gregory, K., "What's Your Flow Control Valve Telling You," *Control Design*, May 2004.



Moore, Ralph L., "Good pH Measurements in Bad Process Streams", Instruments and Control Systems, December 1990.

Rushton C. and Bottom A., "Measuring pH in Low Conductivity Waters", Kent Technical Review, Great Britain, No. 24, Coden: KTTRAH, March 1979.

# **Appendix B: Questions and Answers**



pump, should the reagent be added to the spray as it enters the column, to the sump, or to the suction of the circulation pump?

- 8.6. Why should a linear reagent demand controller be used for adaptive control?

## Chapter 1 Answers

- 1.1. The hydrogen ion concentration must decrease by 10 to the fifth power. Since the hydrogen ion concentration is proportional to the acid flow for a strong acid and base system, the acid flow must also decrease by the same factor.
- 1.2. The slope of the titration curve, and hence the pH process gain, is less at 1 than at 6 pH so that changes in net acid or base concentration along the abscissa due to control valve stick-slip translate into smaller pH changes.
- 1.3. The pH process gain increases by a factor of 10 to the fifth power since the difference between 1 and 6 pH is 5 pH and the pH gain increases by a power of 10 for each pH unit increase towards 7 pH for a strong acid and strong base system.
- 1.4. The titration curve slope and hence the pH process gain is greatest at 7 pH for a strong acid and strong base system at 25°C.

## Chapter 2 Answers

- 2.1. The influent density is 1100 gm per liter for a 1.1 specific gravity. The molecular weight is 40.01 per Table 2-3a. The valence or charge of sodium hydroxide is 1 per Table 2-2a. Equation 2-1e is solved for the weight fraction of sodium hydroxide in the influent and multiplied by 100%.

$$X_{ii} = \frac{M * N}{z * d} = \frac{40.01 * 2.75}{1 * 1100} = 0.1$$

weight percent = 0.1 \* 100% = 10%

- 2.2. The hydrochloric acid concentration equals the sodium hydroxide concentration in the effluent for complete neutralization since they are both fully ionized. The effluent density is 1080 gm per liter for a 1.08 specific gravity. The molecular weight of hydrochloric acid is 36.46 and the molecular weight of sodium hydroxide is 40.01 per Table 2-3a. The valence or charge of hydrochloric acid and sodium hydroxide is 1 per Table 2-1a. The equation from question 2-1 is ratioed for the weight fraction of hydrochloric acid to sodium

hydroxide in the effluent. Equation 2-1i is used to calculate the required reagent flow in kg per minute.

$$X_{re} = \frac{M_r * N_r}{z_r * d}$$

$$X_{ie} = \frac{M_i * N_i}{z_i * d}$$

Since  $N_r = N_i$  and  $z_r = z_i$ :

$$X_{re} / X_{ie} = M_r / M_i = 36.46 / 40.01 = 0.9125$$

$$F_r = \frac{X_{re} * X_{ii}}{X_{ie} * X_{rr}} * F_i = 0.9125 * \frac{0.10}{0.20} * 100 = 45.6 \text{ kg per minute}$$

- 2.3. At 7 pH and for a  $pK_w$  equal to 14, the concentration of hydrogen ions equals the concentration of hydroxyl ions. The concentration of acid ions must then equal the concentration of base ions. Since a strong acid or base is completely ionized, the concentration of the acid or base must be equal if the solution temperature is 25°C.
- 2.4. Since a weak acid or base is partially ionized, the concentration of the acid only equals the concentration of the base if the acid dissociation constants are equal to the base dissociation constants in addition to the solution temperature being 25°C.
- 2.5. At 50°C, the  $pK_w$  is 13.26 per Table 2-3b. Equation 2-3l shows that for equal hydrogen and hydroxyl ion concentrations, the hydrogen ion concentration is equal to the square root of the ionic product or the pH is equal to half of the  $pK_w$ .

$$pH = pK_w / 2 = 13.26 / 2 = 6.63$$

## Chapter 3 Answers

- 3.1. The systems ranked from least to greatest slope and hence reagent sensitivity and pH process gain at 6 pH are:
  - (1) weak acid and weak base
  - (2) weak acid and strong base
  - (3) strong acid and weak base
  - (4) strong acid and strong base
- 3.2. The best pH set point would be at a pH equal to the  $pK_a$  since this is the midpoint of the flat portion of the titration curve.



- 3.3. The caustic solution would absorb carbon dioxide, which would add a buffering effect that may not be in the process, the number of data points may be insufficient near the equivalence point due to the steep slope, and the error at the high pH end of the scale may be different than the field due to a sodium ion error.
- 3.4. The interval-halving search method will always converge since there is only one zero crossing of the charge balance if the pH is within the original search interval selected and if the arithmetic precision of the computer is sufficient for the pH system.
- 3.5. The laboratory titration curve would be more accurate due to the uncertainty as to the activity coefficients from high ion interaction.
- 3.6. The lime would not be completely dissolved with its ions into solution.

## Chapter 4 Answers

- 4.1. The internal fill is at 6 pH per Equation 2-2b so that 6 instead of 7 pH should be used in Equation 4-1i, and the isopotential point is shifted from 7 to 6 pH.
- 4.2. The slope is the absolute temperature term in Equation 4-1i that is multiplied by the deviation of the pH from the isopotential point.  

$$\text{slope} = 0.1984 \cdot (T + 273.16) = 0.1984 \cdot (100 + 273.16) = 74.04 \text{ mV per pH}$$
- 4.3. An erratic reading (noise) can be caused by measurement bulb abrasion, dehydration, or etching, pure water, or gas bubbles.
- 4.4. A slow response can be caused by measurement bulb abrasion, dehydration, etching, or coating, non-aqueous solutions, or low sample velocity.
- 4.5. The alkalinity error causes the shortened span or bending over of the millivolt versus pH line at the high end of the scale.
- 4.6. A constant pH reading is most likely due to a broken measurement electrode.
- 4.7. The measurement electrode terminal could be shorted to ground or to the reference electrode terminal, the pH meter switch could be in the standby position, or the circuit could be open due to a broken electrode wire or a complete nonconductive coating of either electrode.
- 4.8. Since no known electrode failure could cause such an extreme millivolt, the source must be either a concentrated strong acid or an open circuit in the transmitter output.
- 4.9. The transportation delay is calculated via Equation 4-7b where volume is the product of area and length after the cross-sectional area is

From Figure 6-2b:

$$E_r = 80 * \frac{B}{A} = 80 * \frac{0.1}{0.8} = 1\%$$

$$S_s = 0.5 * E_r = 0.5\%$$

- 6.2. The reagent error is doubled and the pH error is increased by a factor of 20.
- 6.3. If the leak is caused by a stuck stem, a valve position indicator in the control room could be used but valve position transmitters and indicators are rarely installed. If the leak is caused by valve seat corrosion or erosion, the leak is difficult to detect and can result in significant waste of both reagents. A monitoring of the pH controller output would show a larger than normal base reagent demand. If the influent flow is stopped and the set point is above the acid reagent pH, the base reagent valve will remain open. An acid and base reagent system should have flowmeters to detect leaks.
- 6.4. Equations 6-4b and 6-4c are used to calculate that the signal portions are 79.2% and 19.8% for the acid and base valves, respectively. One of the valve actions must be reversed since the reagents have opposite effects on the pH measurement. If the acid valve is reversed, the resulting split range works as shown in the table below, which shows a split range gap of 1% at the transition point.

$$S_1 = 99 * \frac{X_1}{X_1 + X_2} = 99 * \frac{1000}{1000 + 250} = 99 * 0.8 = 79.2\%$$

$$S_2 = 100 - G - S_1 = 100 - 1 - 79.2 = 19.8\%$$

Controller Output	Acid Valve Position	Base Valve Position
0%	00%	0%
39.6%	50%	0%
79.2%	0%	0%
80.2%	0%	0%
90.1%	0%	50%
100%	0%	100%

- 6.5. The valve dead time from dead band is approximately equal to the valve dead band divided by the rate of change of valve signal. For 5% valve dead band and a 0.1% per second signal rate of change of controller output, the dead time is 50 seconds.



## Appendix C

### Glossary of pH Control System Terminology

**activity** - Ratio of escaping tendency of the component in solution to that of a standard state. The ion concentration multiplied by an activity coefficient is the ion activity.

**association** - The combining of ions into larger ion clusters in concentrated solutions.

**asymmetry potential** - The difference in potential between the inside and outside pH sensitive glass layers when they are both in contact with 7 pH solutions. It is caused by deterioration of the pH sensitive glass layers or contamination of the internal fill of the measurement electrode.

**dissociation** - The breaking apart of a molecule into its component ions in a solution.

**diffusion** - The movement of ions from areas of high concentration to low concentration.

**equivalence point** - Point on the titration curve where the acid ion concentration equals the base ion concentration.

**ionic strength** - Effective strength of all ions in a solution that is equal to the sum of one half of the product of the individual ion concentration and their ion valence or charge squared for dilute solutions.

**isopotential point** - Point on the millivolt versus pH plot at which a change in temperature has no effect. It is at 7 pH and 0 mV for a glass electrode unless shifted by the standardization and meter zero adjustments or an electrode asymmetry potential.

**migration** - The movement of ions from an area of the same charge to an area of opposite charge.

**molal units** - Concentration units defined as the number of gm-moles per 1000 gm of solvent.

**molar units** - Concentration units defined as the number of gm-moles of the component per liter of solution.

**moles** - Number of molecular weights, which is the weight of the component divided by its molecular weight.

**neutral point** - Point on the titration curve where the hydrogen ion concentration equals the hydroxyl ion concentration.

**normality** - Concentration units defined as the number of gram-ions of replaceable hydrogen or hydroxyl groups per liter of solution. A shorter notation of gram-equivalents per liter is frequently used.

**lab titration curve** - A plot with pH as the ordinate and a ratio of reagent added per unit of sample as the abscissa.



# **Appendix D: Review of Algebra with Logarithms**

## Appendix D

### Review of Algebra with Logarithms

$$\log (m * n) = \log (m) + \log (n)$$

$$\log (m / n) = \log (m) - \log (n)$$

$$\log (10^p) = p * \log (10) = p \text{ antilog } (p) = p$$

$$\log (m * 10^p) = \log (m) + p$$

Therefore, to convert from hydrogen activity to pH: (The same procedure is used to convert from an acid dissociation constant to a negative base 10 logarithmic  $pK_a$ ).

$$pH = -\log (a_H)$$

$$pH = -\log (m * 10^{-p})$$

$$pH = -[\log (m) - p]$$

For example, if the hydrogen activity is 0.0003:

$$pH = -\log (3 * 10^{-4})$$

$$pH = -[\log (3) - 4] = 3.523$$

And to convert back from pH to hydrogen activity:

$$a_H = -\text{antilog } (pH)$$

$$a_H = -\text{antilog } [-(\log (m) - p)]$$

$$a_H = m * 10^{-p}$$

For example, if the pH is 3.523:

$$a_H = -\text{antilog } [-(0.477 - 4)]$$

$$a_H = -\text{antilog } [-(\log (3) - 4)]$$

$$a_H = 3 * 10^{-4}$$



# **Appendix E: Control Talk Column Excerpts**

## Appendix E

### Control Talk Column Excerpts

#### April 2004 Control Talk

##### “Size does Matter”

**Greg McMillan and Stan Weiner**

**Greg:** We are right in the thick of things here in Naples, Florida doing important stuff such as swamp surfing and reviewing the replies to the February puzzler that asked why a 98% sulfuric pH control valve went wide open when the fluid temperature dropped from 80°F to 50°F.

**Stan:** We got some replies from readers who have been with us through thick and thin such as Mark Chatterton, Dick Morris, and Hunter Vegas who raised the distinct possibility that the drop in fluid temperature raised the solution pH, which in turn caused the controller to increase the opening of the acid reagent valve.

**Greg:** The phrase “in turn” is effective because you don’t need to be more specific unless you are talking about car racing.

**Stan:** These guys did go into more detail and Dick even got into the chemistry.

**Dick:** As the temperature dropped, the equilibrium constant of sulfuric acid decreased, which decreased the number of ions dissociated and increased the number of molecules required.

**Greg:** Dave Mills and Robert Ecklund hit with full throttle the answer spinning in our minds like a car out of control. (We promise this is our last attempt to sound more like “Car Talk”). While sulfuric is not as “thick as a brick”, its high viscosity is a problem.

**Dave:** When 98% sulfuric acid goes from 80°F to 50°F, its viscosity goes from about 20 cP to about 35 cP. Considering that this is a reagent line where the flow rate is relatively low, the flow is probably laminar in nature. For laminar flow, the actual  $C_v$  of a control valve is a strong function of viscosity. Thus, as the viscosity increases, the actual  $C_v$  of the valve decreases and the valve has to open more to obtain the same flow rate. In this case, the viscosity change is great enough that even when the valve is fully open, it cannot achieve a high enough flow.



**Stan:** If the temperature had dropped some more, it could have frozen as suggested by Barb Alexander, Keith Jones, and Derek Rainwaters. Small valves can have big problems.

**Greg:** The small valves typically used in pH control are more prone to improper sizing, irregular flow characteristics, greater stick-slip, and plugging. Here size does matter because most of these problems originate from extremely small Reynolds Numbers, clearances, and stem diameters.

**Stan:** Some reagents such as 98% sulfuric have a viscosity so high, starting the injection flow is like trying to get ketchup out of a bottle. Even worse is operation in the transition region where the flow for a particular valve position has poor reproducibility because normally insignificant disturbances such as microscopic changes in roughness or small vibrations can trigger a switch between turbulent and laminar flow.

**Greg:** If you also consider the possibility of a significant distortion of the inherent flow characteristic caused by machining tolerances that are an appreciable portion of the clearances for such tiny trim sizes, the scene is set up for an unknown and extreme nonlinearity. Tiny clearances can pose all sorts of problems because small particles and coatings cause plugging and sticking. The low flow velocities at the surface that are normally associated with laminar flow makes the likelihood of coating much greater.

Finally, tiny stems are likely to be bent from the normal handling both before and after installation. Slight deflections of the stem can cause huge amounts of stick-slip.

**Stan:** What good is a control valve if you can't drop it or step on it? In order to avoid these and other fates that might make you and the trend of a loop as miserable as the attitude of a teenager, we offer the following "Top Ten Signs of a Valve Problem".

### **Top Ten Signs of a Valve Problem**

10. The pipe fitters are complaining about trying to fit a 1-inch valve into a 10-inch pipe.
9. You bought the valve suppliers' "monthly special."
8. A butterfly disc won't open because the lined pipe ID is smaller than the disk OD.
7. The maintenance department personally put the valve on your desk.
6. A red slide ruler was used to size a green valve.

parameters you can adjust on the fly to compensate for changes in the shape of the titration curve.

**Tom:** Some other solutions that may work, and were not given as options, would be the error squared algorithm which would allow the gain to vary based on the error. Another option would be a non-linear gain modifier, which is also similar to an error squared algorithm. We have used these successfully on similar situations.

**Stan:** The fuzzy logic and error squared controllers are both nonlinear controllers whose control action increases with deviation from set point, which compensates for a decreasing slope and hence process gain as you move away from the neutral point. If the system is a strong acid and base, the more aggressive error squared algorithm might be the best choice. For a slowly changing nonlinearity that occurs for pH control of waste in a well-mixed vessel, the best bet is an adaptive PID controller that updates a gain scheduler based on operating point. Mike DeKrey also had a point that has saved waste neutralization projects a lot in reagent costs.

**Mike:** You are trying to control at the point where the least input change causes the greatest output change. Move the aim to a higher (or lower, depending upon the next step) pH and use a controller that slows down the rate of addition as you get close. Remember pH is a log scale of hydrogen ion concentration (activity), so pH 8 is a millionth mole per liter excess caustic, pH 11 is a thousandth mole per liter excess caustic.

**Greg:** This discussion has been just a desert for the main course presented in this issue, which brings me to share as an after dinner story my top ten reasons for becoming a control engineer.

### **Greg's Top Ten Reasons for Becoming a Control Engineer**

10. To meet girls. Unfortunately there were none in my class or on my job. I guess I was ahead of my time.
9. To impress girls. Boy was I wrong again. Have you ever tried to describe what you do as a control engineer in a bar?
8. I mistook all those personal ads asking for a "control freak" in the *Riverfront Times* as a career opportunity.
7. It offered a chance to carry photos of my favorite pH electrodes in my wallet. Now I can carry CDs.
6. I thought the control room would be like the bridge of the Starship Enterprise. I didn't find any anti-matter drives but I did get to



## Appendix F

### FORTTRAN Subroutine for Charge Balance Model

SUBROUTINE ZPH3(Y, C, P, W, M, H, PK1, PK2, PK3, N)  
REAL C(N), P(6), W(N), M(N), H(N), PK1(N), PK2(N), PK3(N)

CALCULATED OUTPUTS:

Y IS THE PH WITH OPTIONAL ELECTRODE ERROR

C IS THE CONCENTRATION IN NORMALITY UNITS

DATA INPUTS:

P( 1) IS THE DISSOCIATION CONSTANT FOR WATER

P(2) IS THE ELECTRODE ERROR INDICATOR

P(3) IS THE AVERAGE DENSITY C P(4) IS THE LOWER PH LIMIT

P(5) IS THE UPPER PH LIMIT

P(6) IS THE PH SEARCH ERROR C W IS THE WEIGHT PERCENT

M IS THE MOLECULAR WEIGHT

H IS THE NUMBER OF HYDROGEN OR HYDROXYL IONS

PK1 IS THE FIRST DISSOCIATION CONSTANT

PK2 IS THE SECOND DISSOCIATION CONSTANT

PK3 IS THE THIRD DISSOCIATION CONSTANT

N IS THE TOTAL NUMBER OF ACIDS AND BASES

CALCULATE THE CONCENTRATION OF EACH ACID AND BASE

PKW = P(1)

DO 10 J = 1,N

C(J) = (1000.\*H(J)\*P(3)\*W(J))/M(J)

10 CONTINUE C

C ASSIGN THE UPPER AND LOWER LIMITS OF PH SEARCH

C

PHL = P(4)

PHH = P(5)

C

C CALCULATE THE MIDPOINT PH AND SEARCH ERROR

C

20 PHM = (PHL + PHH)/2.

E = (PHH - PHL)/2.

I = 1

C

C CALCULATE HYDROGEN AND HYDROXYL ION CONCENTRATIONS

C

QE = 10.\*\*(-PHM) - 10.\*\*(PHM - PKW) C

C SET PARAMETER S SIGN AS INDICATOR OF ACID OR BASE

C

DO 30 J = 1,N

S = SIGN(1.,H(J))

C

C CALCULATE EFFECT FIRST DISSOCIATION CONSTANT PARAM

```

C
P1 = 10.**(S*(PHM-PK1(J)))
C
C CALCULATE SECOND AND THIRD DISSOCIATION CONSTANT PARAM
C
IF (ABS(H(J)).GT.1.) P2 = 10.**(S*(PHM - PK2(J)))
IF (ABS(H(J)).GT.2.) P3 = 10.**(S*(PHM - PK3(J)))
C
C CALCULATE THE ACID AND BASE ION CONCENTRATIONS
C
QI = C(J)/(1. + P1)
IF (ABS(H(J)).GT.1.) QI = C(J)*(1. + 0.5*P2)/(1. + P2*(1. + P1))
IF (ABS(H(J)).GT.2.) QI = C(J)*(1. + 0.33*P3*(2. + P2))
$ / (1. + P3*(1. + P2*(1. + P1)))
C
C CALCULATE THE NET CHARGE BALANCE
C
QE = QE + QI
30 CONTINUE
C
C REDUCE THE SEARCH INTERVAL BY ONE HALF
C
IF (QE.GT.0.) I = -1
IF (I.LT.0) PHL = PHM
IF (I.GT.0) PHH = PHM
C
C CHECK ERROR TO REPEAT OR END PH SEARCH
C
IF (E.LT.P(6)) GO TO 40
GO TO 20
C
C CORRECT FOR LOW AND HIGH PH ELECTRODE ERROR
C
40 PHE = 0.0
IF (PHM.GT.1.0) GO TO 50
IF (P(2).EQ.1.0.0R.P(2).EQ.3.0) PHE = -0.049999 + 0.135999*PHM
$ + 0.002000*PHM**2. - 0.01600000*PHM**3.- 0.071999*PHM**4.
50 IF (PHM.LT.8.0) GO TO 60
IF (P(2).EQ.2.0.0R.P(2).EQ.3.0) PHE = 50.64536 - 21.20648*PHM
$ + 3.316879*PHM**2. - 0.2305096*PHM**3.+ I 0.006042*PHM**4.
60 Y=PHM-PHE
RETURN
END

```



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Gregory K. McMillan and Robert A. Cameron

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FAX (919) 549-8288  
E-MAIL [info@isa.org](mailto:info@isa.org)  
[www.isa.org](http://www.isa.org)

ISBN 978-1-934394-43-4  
90000

